



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

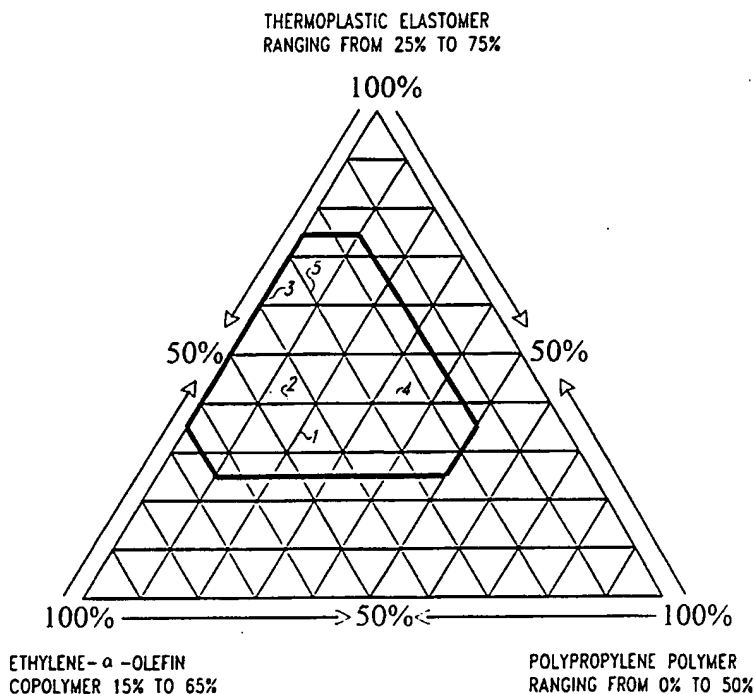
(51) International Patent Classification ⁷ : B65D 39/00, C08J 9/00		A1	(11) International Publication Number: WO 00/26103 (43) International Publication Date: 11 May 2000 (11.05.00)
(21) International Application Number: PCT/US99/25862 (22) International Filing Date: 2 November 1999 (02.11.99) (30) Priority Data: 60/107,145 4 November 1998 (04.11.98) US (71) Applicant (for all designated States except US): SUPREME CORQ, INC. [US/US]; 5901 - South 226th Street, Kent, WA 98032 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): ZECH, Jerome, M., Jr. [US/US]; 5901 - South 226th Street, Kent, WA 98032 (US). PLIMMER, Peter, N. [US/US]; 602 Kilburn Road, Wilmington, DE 19803-1705 (US). (74) Agents: LOOP, Thomas, E. et al.; Seed and Berry LLP, 6300 Columbia Center, 701 Fifth Avenue, Seattle, WA 98104-7092 (US).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

(54) Title: SYNTHETIC CLOSURE FOR BOTTLE-LIKE CONTAINERS

(57) Abstract

The present invention is directed to an easily removable synthetic closure suitable for removable insertion into a bottle or container. In one embodiment, the synthetic closure comprises a thermoplastic elastomer and a metallocene catalyzed ethylene- α -olefin copolymer. In another embodiment, the synthetic closure is made from a composition formulated from the ingredients comprising: a thermoplastic elastomer that comprises a styrenic block copolymer; an ethylene- α -olefin copolymer; a polypropylene polymer; and a blowing agent; and wherein the closure has a Shore A hardness ranging from 60 to 84. The synthetic closure may further comprise an extending oil and/or a processing additive. In alternative embodiments the compositions suitable for forming the synthetic closures of the present invention optionally include thermoplastic elastomer materials such as, for example, thermoplastic polyurethane

elastomers (i.e., TPUs), polyolefin-based thermoplastic elastomers (i.e., TPOs), thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends (i.e., TPVs), thermoplastic polyether ester elastomers, thermoplastic elastomers based on halogen-containing polyolefins, and thermoplastic elastomers based on polyamides.



*(Referred to in PCT Gazette No. 39/2000, Section II)

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LJ	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

SYNTHETIC CLOSURE FOR BOTTLE-LIKE CONTAINERS

TECHNICAL FIELD

The present invention is generally directed to a primary synthetic closure
5 suitable for removable insertion into a bottle or container, and more specifically, to a
synthetic closure comprising a thermoplastic elastomer compounded with an ethylene- α -
olefin copolymer and a polypropylene polymer.

BACKGROUND OF THE INVENTION

Historically, natural cork has been utilized as the primary closure for
10 stopper-type bottle closures. There are, however, several disadvantages associated with
the use of natural cork. For example, natural cork may have variable properties with
respect to, among other things, color, drying, shrinkage or expansion, crumbling,
sticking to containers and seal formation. These features are generally undesirable in
terms of production and consumer costs as well as product performance.

15 As a result of the disadvantages associated with natural cork, numerous
attempts have been made to develop alternatives to natural cork bottle stoppers, such as
the development of synthetic closures. In particular, recent efforts to develop closures
from injection and extrusion plastic processing techniques have encountered numerous
pitfalls, particularly in terms of production cost, product performance, and consumer
20 acceptance. Some of these closures have exhibited a tendency to noticeably taint the
product and/or offer low resistance to oxygen permeation into the container. In
addition, some synthetic closures made from known plastic compositions and
formulations have generally exhibited poor uniformity in terms of size, shape, weight,
and other features important to production, marketing, and performance of synthetic
25 closures.

In the case of injection molding, the plastic compositions are generally
injected into relatively cool molds, leading to the formation of a dense outer skin at the
surface of the closure with a porous, foam-like interior. The composition of the closure,

and the structural relationship between the outer skin and porous core of the closure, are often critical to imparting desired characteristics to the finished closure. Unfortunately, foamed plastic closures often suffer problems due to wrinkling of the outer skin, which can produce leakage fissures between the closure and the container. Other synthetic
5 closures have different sealing problems. For example, some synthetic closures fail to quickly return to normal size after compression, requiring bottles and/or containers to be kept in an upright position for an extended period after insertion of the closure.

One type of synthetic closures is disclosed in U.S. Patent No. 4,363,849 to Paisley *et al.* This patent discloses the production of synthetic closures having a
10 natural cork-like appearance, wherein the synthetic material is a polyolefin, such as an ethylene vinyl acetate copolymer (EVA). However, special injection molding apparatuses are required in which it is necessary to gradually release the air in the cold molding cavity that is displaced by the injected synthetic resin. This is accomplished by means of controlled minimum venting, or other means in order to maintain the
15 heightened pressure (*e.g.*, about 16,000 psi) within the mold. Similarly, U.S. Patent No. 4,188,457 to Throp discloses another plastic composition that is used to form closures for wine bottles. The thermoplastic composition disclosed by this patent also comprises an EVA copolymer, which material, however, is undesirable because it is not able to quickly expand back to its original formed shape after being compressed by, for
20 example, the jaws of a bottling machine. Put simply, an EVA copolymer synthetic closure does not have adequate elastomeric properties which allows it to sealingly engage an opening of, for example, a wine bottle substantially immediately after being inserted therein by means of a bottling machine. This drawback prohibits the wine bottle from being placed in a horizontal position substantially immediately after
25 corking.

Another type of synthetic closure is disclosed in U.S. Patent No. 5,904,965 to Noel *et al.* More specifically, this patent discloses a synthetic closure made by a co-extrusion molding process that produces a continuous rod having a foamed core surrounded by a peripheral non-foamed skin layer. (The continuous rod is
30 then cut into smaller cylinders that constitute individual synthetic closures.) A problem

associated with this type of closure, however, is that there is no protective skin layer at either of its ends. As a result, gas permeation through the foamed core is unimpeded (which may be undesirable for purposes of fine wine making). In addition, the lack of a protective skin layer at the ends of the synthetic closure significantly inhibits the ability to print thereon. As is appreciated by those in the wine industry, for example, it is often desirable to have printed matter (or other embossed/debossed emblems) on the ends of closures.

Still another type of synthetic closure is the kind disclosed in U.S. Patent No. 5,317,047 to Sabate *et al.* This patent discloses, among other things, a composition useful for making synthetic closures, wherein the composition constitutes a mixture of three principal components; namely, (1) powder and particles of natural cork; (2) expandable plastic microspheres of a methyl methacrylate-acrylonitrile copolymer; and (3) a binding agent of a polyurethane or acrylic type. As disclosed, a selected amount of such a three-part composition is introduced into a cylindrical shaped mold, heat is then rapidly applied in order to expand the plastic microspheres thereby causing the composition to fill the mold; and finally the expanded composition is allowed to slowly cool in order to properly set the binding agent.

The resulting synthetic closure made in accordance with U.S. Patent No. 5,317,047 to Sabate *et al.* has many characteristics consistent with that of natural cork; however, it does not possess a protective outer skin like that of many other types of synthetic closures. Because there is no protective outer skin, the resulting synthetic closure suffers from at least two drawbacks. First, the synthetic closure is substantially less durable than a synthetic closure having a protective outer skin (e.g., the pulling action associated with removing the synthetic closure from a bottle using a traditional corkscrew may cause cracking and disintegration that shortens the synthetic closure's useful life). Second, the synthetic closure is more amenable to "scoring" when compressed by the jaws of a bottling machine than a synthetic closure encapsulated by a protective outer skin.

To date, one of the most successful synthetic closures, which overcomes many of the disadvantages associated with natural cork and other prior art synthetic

closures, are the synthetic closures manufactured by Supreme Corq (Kent, Washington U.S.A.). Specifically, U.S. Patent Nos. 5,480,915, 5,496,862, 5,692,629, 5,710,184, and 5,855,287 all to Burns and owned by Supreme Corq (and are all expressly incorporated herein by reference), disclose various synthetic closures for removable
5 insertion into bottles and containers. These synthetic closures are made from formulations that comprise a "thermoplastic elastomer" material, wherein the thermoplastic elastomer preferably comprises a styrene block copolymer. Such synthetic closures generally have outer skins with a porous, foam-like interior, and have proved to be a significant improvement over both natural corks and other synthetic
10 closure assemblies. Moreover, the thermoplastic elastomer formulations first invented by Supreme Corq are amenable to both injection and extrusion molding.

Although the synthetic closures manufactured by Supreme Corq are superior in many respects as compared to other types of bottle or container closures, technical problems still exist with these and other synthetic closures. For example, and
15 although some synthetic closures can permanently retain printed matter on their surfaces, printed matter on known synthetic closures is generally too easily removed by frictional forces. That is, the frictional forces associated with removing and reinserting a synthetic closure into a bottle or container causes undesirable removal of the printed matter. In short, the ink that constitutes the printed matter on the closure rubs off too
20 easily (thereby obscuring the printed subject matter). Another problem relates to production costs; for example, many of the existing materials used in synthetic closures are relatively expensive.

Accordingly, and while significant advances have been made in the field of synthetic closures for removable insertion into bottles and containers, there is still a
25 need in the art for novel and improved synthetic closures and manufacturing processes relating thereto. The present invention fulfills these needs and provides for further related advantages.

SUMMARY OF THE INVENTION

In brief, the present invention is directed to an easily removable synthetic closure suitable for removable insertion into a bottle or container. In one embodiment, the synthetic closure comprises a thermoplastic elastomer and a metallocene catalyzed ethylene- α -olefin copolymer. In another embodiment, the synthetic closure is made from a composition formulated from the ingredients comprising: a thermoplastic elastomer that comprises a styrenic block copolymer; an ethylene- α -olefin copolymer; a polypropylene polymer; and a blowing agent; and wherein the closure has a Shore A hardness ranging from 60 to 84. The synthetic closure may further comprises an extending oil and/or a processing additive. Without necessarily prescribing to any particular scientific theory, it is believed that the relatively higher crystallinity associated with some of these ingredients (which comprise the inventive closures) allows for better retention of printed matter because surface impinged ink particles are believed to be better trapped within the polymeric matrix associated with the skin portion of the closure.

In some embodiments, the styrenic block copolymer is a styrene-ethylene/butylene-styrene block copolymer, a styrene-ethylene/propylene-styrene block copolymer, a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, or a mixture thereof. Preferably, the styrenic block copolymer is a styrene-ethylene/butylene-styrene block copolymer and a styrene-ethylene/propylene-styrene block copolymer, or a mixture thereof. Further preferably, the styrenic block copolymer is a styrene-ethylene/butylene-styrene block copolymer.

In other embodiments, the ethylene- α -olefin copolymer is an ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, or a mixture thereof. Preferably, the ethylene- α -olefin copolymer is an ethylene-octene copolymer.

In still other embodiments, the polypropylene polymer is a syndiotactic polypropylene polymer and a isotactic polypropylene polymer, or a mixture thereof. Preferably, the polypropylene polymer is a syndiotactic polypropylene polymer.

In still further embodiments, the synthetic closure is made from a composition comprising: a thermoplastic elastomer that comprises a styrenic block copolymer, wherein the thermoplastic elastomer ranges from 10% to 95% by weight of the composition; a first polymer that comprises polypropylene, wherein the first
5 polymer ranges from 0% to 25% by weight of the composition; a second polymer that comprises an ethylene- α -olefin copolymer, wherein the second polymer ranges from 5% to 60% by weight of the composition; and an extending oil that comprises a polyolefin, wherein the extending oil ranges from 0% to 35% by weight of the composition.

10 In addition to the above, the present invention is also directed to a synthetic closure adapted to sealingly engage a cylindrical opening of a wine bottle, wherein the synthetic closure comprises a first thermoplastic vulcanizate. The first thermoplastic vulcanizate may be a dynamic vulcanized blend that includes an olefin rubber and a polyolefin resin. Alternatively, the first thermoplastic vulcanizate may be
15 a dynamic vulcanized blend that includes an ethylene-propylene-diene terpolymer elastomer and a polypropylene and/or a polyethylene.

The present invention is also directed to a cylindrical shaped synthetic closure adapted for removable insertion into an opening of a wine bottle, wherein the synthetic closure has an inner foamed core structure surrounded by an outer skin layer
20 that is of the same or different material than the inner foamed core structure, and wherein the synthetic closure is further adapted to sealingly engage the opening of the wine bottle, wherein the synthetic closure comprises a polymeric composition that includes a thermoplastic elastomer and a metallocene catalyzed ethylene- α -olefin copolymer. In these embodiments, the thermoplastic elastomer is one or more of an
25 ethylene- α -olefin copolymer thermoplastic elastomer, a thermoplastic polyurethane elastomer, a polyolefin-based thermoplastic elastomer, a thermoplastic polyether ester elastomer, and a styrene block copolymer thermoplastic elastomer. Moreover, the α -olefin component of the ethylene- α -olefin copolymer thermoplastic elastomer ranges from about 2% to 30% by weight of the copolymer, wherein the ethylene- α -
30 olefin copolymer thermoplastic elastomer is a metallocene catalyzed ethylene- α -olefin

copolymer selected from one or more of an ethylene-butene copolymer, an ethylene-hexene copolymer, and an ethylene-octene copolymer.

The present invention is further directed to a cylindrical shaped synthetic closure adapted for removable insertion into an opening of a wine bottle, wherein the synthetic closure has an inner foamed core structure surrounded by an outer skin layer that is of the same or different material than the inner foamed core structure, and wherein the synthetic closure is further adapted to sealingly engage the opening of the wine bottle, wherein the synthetic closure comprises a thermoplastic polyurethane elastomer. In these embodiments, the thermoplastic polyurethane elastomer may comprise a plurality of soft flexible segments and a plurality of hard segments, wherein the soft flexible segments comprise one or more long-chain polyols having an average molecular mass ranging from of 60 to 4,000 atomic mass units, and wherein the hard segments comprise one or more polyisocyanates. More specifically, the soft flexible segments may be hydroxyl terminated polyesters or hydroxyl terminated polyethers, and the hard segments may be selected from the group consisting of 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 1,4-benzene diisocyanate, *trans*-cyclohexane-1,4-diisocyanate, and 1,5-naphthalene diisocyanate.

The present invention is also directed to methods for manufacturing synthetic closures (as well the synthetic closures made therefrom), methods that include injection, extrusion, and co-extrusion processing techniques. In this regard, the present invention includes a method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of: compounding a polymeric composition from the ingredients comprising a styrene block copolymer thermoplastic elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer; combining the polymeric composition with a blowing agent under heat to yield a feedstock; injecting the feedstock into a mold having a cylindrical shape; and cooling the mold to form the synthetic closure.

In another embodiment, the present invention is directed to a method for manufacturing a synthetic closure adapted for removable insertion and sealable

engagement with an opening of a wine bottle, comprising the steps of: combining a polymeric composition that comprises a thermoplastic vulcanizate with a blowing agent under heat to yield a feedstock; injecting the feedstock into a mold having a cylindrical shape; and cooling the mold to form the synthetic closure.

5 In still another embodiment, the present invention is directed to a method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of: combining a polymeric composition that comprises a thermoplastic polyurethane elastomer and/or a polymeric composition that comprises a styrene block copolymer thermoplastic
10 elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer, with a blowing agent under heat to yield a feedstock; injecting the feedstock into a mold having a cylindrical shape; and cooling the mold to form the synthetic closure.

In still further embodiments, the present invention is directed to a method for manufacturing a synthetic closure adapted for removable insertion and
15 sealable engagement with an opening of a wine bottle, comprising the steps of: compounding a polymeric composition from the ingredients comprising a styrene block copolymer thermoplastic elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer; combining the polymeric composition with a blowing agent under heat to yield a feedstock; extruding or co-extruding the feedstock through a
20 circular die to form a rod; cooling the rod to yield a cooled rod; and cutting the cooled rod to form the synthetic closure.

The present invention is also directed to a wine bottle in combination with any one of the synthetic closures disclosed herein.

The above-discussed synthetic closures and methods for manufacturing
25 the same, as well as various other related aspects, will be evident to those skilled in the art upon reference to the following detailed description and related Figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts a front isometric view of a synthetic closure suitable for removable insertion into a wine bottle, the synthetic closure evidencing a marbled surface texture, an embossed symbol on an end, and printing on its side.

5 Figure 2 depicts a front side elevational view of the synthetic closure of Figure 1.

Figure 3 depicts a top plan view of the synthetic closure of Figure 1.

Figure 4A is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 15 times) taken substantially along line 2-2 of Figure 2 showing the
10 inner foam structure and outer skin of an exemplary injection molded synthetic closure.

Figure 4B is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 30 times) taken substantially along line 2-2 of Figure 2 showing the inner foam structure and outer skin of an exemplary injection molded synthetic closure.

Figure 4C is an enlarged cross-sectional partial view (*i.e.*, magnified
15 approximately 100 times) taken substantially along line 2-2 of Figure 2 showing the inner foam structure and outer skin of an exemplary injection molded synthetic closure.

Figure 5A is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 15 times) showing the inner foam structure and outer skin of an exemplary first extrusion molded synthetic closure.

20 Figure 5B is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 30 times) showing the inner foam structure and outer skin of the exemplary first extrusion molded synthetic closure of Figure 5A.

Figure 5C is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 100 times) showing the inner foam structure and outer skin of the
25 exemplary first extrusion molded synthetic closure of Figure 5A.

Figure 6A is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 15 times) showing the inner foam structure and outer skin of an exemplary second extrusion molded synthetic closure.

Figure 6B is an enlarged cross-sectional partial view (*i.e.*, magnified
30 approximately 30 times) showing the inner foam structure and outer skin of the exemplary second extrusion molded synthetic closure of Figure 6A.

Figure 6C is an enlarged cross-sectional partial view (*i.e.*, magnified approximately 100 times) showing the inner foam structure and outer skin of the exemplary second extrusion molded synthetic closure of Figure 6A.

Figure 7A is a perspective top view of a first representative synthetic
5 cork having a hard plastic top coupled to a elastomeric shaft in accordance with the present invention.

Figure 7B is a cross-sectional view taken substantially along line 7B-7B of Figure 7A showing the hard plastic top having an extension that extends downwardly into the elastomeric shaft.

10 Figure 7C is a cross-sectional view taken substantially along line 7C-7C of Figure 7B showing a portion of the hard plastic top encircling the shaft, and a portion of the shaft encircling the extension of the hard plastic top.

Figure 8A is a perspective top view of a second representative synthetic cork having a hard plastic top coupled to a elastomeric shaft in accordance with the
15 present invention.

Figure 8B is a cross-sectional view taken substantially along line 8B-8B of Figure 8A showing the hard plastic top having an extension that extends downwardly into the elastomeric shaft.

Figure 8C is a cross-sectional view taken substantially along line 8C-8C
20 of Figure 8B showing a portion of the hard plastic top encircling the shaft, and a portion of the shaft encircling the extension of the hard plastic top.

Figure 9A is a perspective top view of a third representative synthetic cork having a hard plastic top coupled to a elastomeric shaft in accordance with the present invention.

25 Figure 9B is a cross-sectional view taken substantially along line 9B-9B of Figure 9A showing the hard plastic top having an extension that extends downwardly into the elastomeric shaft.

Figure 9C is a cross-sectional view taken substantially along line 9C-9C of Figure 9B showing a portion of the hard plastic top encircling the shaft, and a portion
30 of the shaft encircling the extension of the hard plastic top.

Figure 10 is a triangular diagram showing the composition of a polymeric material in accordance with an embodiment of the present invention, wherein the polymeric material includes a thermoplastic elastomer, an ethylene- α -olefin copolymer, a polypropylene polymer, and wherein the relative amounts on a weight percent basis of the thermoplastic elastomer, the ethylene- α -olefin copolymer, and the polypropylene polymer vary with one another as set forth.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the present invention is generally directed to a primary synthetic closure suitable for insertion into and subsequent removal from a bottle or container, and more specifically, to a synthetic closure comprising a thermoplastic elastomer optionally compounded with a metallocene catalyzed ethylene- α -olefin copolymer and/or a polypropylene polymer (as well as various processing additives). In one embodiment, the thermoplastic elastomer comprises a styrenic block copolymer compounded with an ethylene-octene copolymer and a high crystallinity polypropylene. In another embodiment, the thermoplastic elastomer comprises a thermoplastic elastomer vulcanizate. In further embodiments, the thermoplastic elastomers of the present invention are optionally compounded with one or more other polymers to yield a composition suitable for forming a primary synthetic closure adapted for sealable engagement and removable insertion into a bottle or container. In still further embodiments, the thermoplastic elastomers of the present invention are blended together with natural cork particles to yield a composition suitable for forming a primary synthetic closure adapted for sealable engagement and removable insertion into a bottle or container. The various thermoplastic elastomers blends disclosed herein are amenable to, among other things, injection, extrusion, and co-extrusion processing techniques.

More specifically, it has been discovered that synthetic closures made from a thermoplastic elastomer optionally compounded with a metallocene catalyzed ethylene- α -olefin copolymer and/or a polypropylene polymer have highly desirable properties and characteristics. For example, it has been surprisingly discovered that,

among other things, such synthetic closures are better able to retain printed matter on their respective surfaces. Without necessarily prescribing to any particular scientific theory, it is believed that the relatively higher crystallinity associated with some of the above-identified ingredients allows for better surface retention of printed matter, because surface impinged ink particles are believed to be better trapped within the polymeric matrix associated with the skin portion of the closure. It is also believed that such synthetic closures are in many ways more resilient (*e.g.*, less amenable to scoring) than existing synthetic closures. In addition, the synthetic closures of the present invention are, in general, relatively less expensive to produce than many of the existing types of synthetic closures.

Because the many embodiments of the present invention encompass a wide range of possible compositions - particularly with respect to ingredients such as, for example, thermoplastic elastomers, metallocene catalyzed ethylene- α -olefin copolymers, polypropylene polymers, and natural cork particles - this Detailed Description of the Invention has been further sub-divided into eight subsections; namely: (1) Overview of Polymer Nomenclature and Theory; (2) Suitable Thermoplastic Elastomers; (3) Suitable Ethylene- α -olefin Copolymers; (4) Suitable Polypropylene Polymers; (5) Suitable Additives; (6) Exemplary Compounding Techniques; (7) Exemplary Synthetic Closure Manufacturing Processes; and (8) Alternative T-Shaped Closure Embodiments. These subsections are followed by Examples. In addition, it is to be understood that although many specific details of certain embodiments of the present invention are set forth below and in the accompanying Figures, the present invention may have additional embodiments, and the invention may be practiced without several of the details described herein.

25

1. Overview of Polymer Nomenclature and Theory

For purposes of clarity, a brief review of polymer nomenclature is provided to aid in the understanding of the present invention. In general, a polymer is a macromolecule (*i.e.*, a long chain molecular chain) synthetically derived from the

30

polymerization of monomer units or which exists naturally as a macromolecule (but which is still derived from the polymerization of monomer units). The links of the molecular chain are the monomer units. For example, polypropylene is a polymer derived from the monomer propylene (CH_2CHCH_3). More specifically, polypropylene is a "homopolymer" - that is, a polymer consisting of a single repeating unit, namely, the monomer propylene (CH_2CHCH_3).

In contrast, a "copolymer" is a polymer containing two (or more) different monomer units. A copolymer may generally be synthesized in several ways. For example, a copolymer may be prepared by the copolymerization of two (or more) different monomers. Such a process yields a copolymer where the two (or more) different monomers are randomly distributed throughout the polymer chain. These copolymers are known as "random copolymers." Alternatively, copolymers may be prepared by the covalent coupling or joining of two homopolymers. For example, the covalent coupling of one homopolymer to the terminus of a second, different homopolymer provides a "block copolymer." A block copolymer containing homopolymer A and homopolymer B may be schematically represented by the following formula: $(\text{A})_x(\text{B})_y$, where $(\text{A})_x$ is a homopolymer consisting of x monomers of A, $(\text{B})_y$ is homopolymer consisting of y monomers of B, and wherein the two homopolymers are joined by a suitable covalent bond or linking spacer group. While the above formula illustrates a block copolymer having two block components (*i.e.*, a "di-block copolymer"), block copolymers may also have three or more block components (*e.g.*, a "tri-block copolymer" schematically represented by the formula $(\text{A})_x(\text{B})_y(\text{A})_x$ or simply A-B-A, as well as a "multiblock copolymer" schematically represented by the formula $\{\text{A-B}\}_n$).

As noted above, exemplary thermoplastic elastomer materials (*i.e.*, TPEs) of the present invention include, but are not limited to, any one or combination of the following: thermoplastic polyurethane elastomers (*i.e.*, TPUs), polyolefin-based thermoplastic elastomers (*i.e.*, TPOs), thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends (*i.e.*, TPVs), thermoplastic polyether ester elastomers, thermoplastic elastomers based on halogen-containing polyolefins,

thermoplastic elastomers based on polyamides, and styrene based thermoplastic elastomers. As is appreciated by those skilled in the art, many of these materials may be characterized (unlike conventional single-phase thermoplastic materials) as having one or more copolymers that comprise a major proportion of a soft segment and a minor
5 proportion of a hard segment so as to result in a composition having a two-phase morphology. Because of this unique chemical structure, such segmented thermoplastic elastomers provide for several of the advantages associated with the present invention.

Stated somewhat differently and without necessarily prescribing to any specific scientific theory, it is believed that many of the thermoplastic elastomers of the
10 present invention possess unique thermal and mechanical properties because they consists of hard segments that have a high glass transition temperature (*i.e.*, T_g) or melting temperature (T_m) alternating with soft segments that have a low T_g (<<room temperature). In addition to these constraints, the hard and soft segments are generally chosen such that the free energy of mixing is positive. As such, the mutual
15 incompatibility of the segments induces microphase separation in the solid state. The hard segments tend to aggregate to form glassy or semicrystalline hard domains interspersed in a continuous soft segment matrix (hence, a two-phase morphology). The boundaries between these two phases are not well defined because there exists some degree of forced compatibility due to the relatively short average chain lengths and
20 molecular weight distributions (*i.e.*, generally below 4,000 atomic mass units) associated with each of the two types of segments.

In addition to the foregoing and as further appreciated by those skilled in the art, the soft segments contribute to the flexibility and extensibility of the thermoplastic elastomer, whereas the glassy or semicrystalline domains of the hard
25 segments serve as physical crosslinks that impedes chain slippage and viscous flow. Because the crosslinks associated with the hard segments are physical in nature (in contradistinction to the chemical bonds found in vulcanized rubber), they are thermally reversible. As such, heating above the softening or melting point of the hard segment causes the hard domains to disassociate and become fluid. Without the hard segment tie
30 points, the thermoplastic elastomer is able to flow, and therefore can be melt processed

in conventional thermoplastic processing equipment, such as, for example, conventional injection molding, extrusion molding, blow molding, and solution casting processing equipment.

Moreover, it is to be understood that the polymer chains associated with the soft and hard segments associated with the above identified thermoplastic elastomers may be synthesized with any number of monomer units - so as to range from short to long - wherein the soft and hard segment chain lengths define, in large part, the physical properties of the thermoplastic elastomer. The lengths of the soft and hard segments notwithstanding, any of the thermoplastic elastomer materials (as well as various combinations thereof) classified-above may be used to produce the primary synthetic closures of the present invention. For purposes of added clarification, the several different classifications of the above-identified thermoplastic elastomer materials are more fully identified and described below.

15

2. Suitable Thermoplastic Elastomers

As noted above, exemplary thermoplastic elastomer materials (*i.e.*, TPEs) of the present invention include, but are not limited to, any one or combination of the following: thermoplastic polyurethane elastomers (*i.e.*, TPUs), polyolefin-based thermoplastic elastomers (*i.e.*, TPOs), thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends (*i.e.*, TPVs), thermoplastic polyether ester elastomers, thermoplastic elastomers based on halogen-containing polyolefins, thermoplastic elastomers based on polyamides, and styrene based thermoplastic elastomers.

The thermoplastic polyurethane elastomers (*i.e.*, TPUs) of the present invention are generally made from long-chain polyols with an average molecular weight of 60 to 4,000, chain extenders with a molecular weight of 61 to 400, and polyisocyanates. Within the genus of TPUs, the soft flexible segments generally comprise either hydroxyl terminated polyesters or hydroxyl terminated polyethers, whereas the hard segments generally comprise 4,4'-diphenylmethane diisocyanate. The

30

hard segments may, however, comprise hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 1,4-benzene diisocyanate, *trans*-cyclohexane-1,4-diisocyanate, and 1,5-naphthalene diisocyanate. As is appreciated by those skilled in the art, the characteristics of the hard
5 segment and to a large extent the physical properties of the TPU are generally determined by the choice of the polyisocyanate and its associated chain extender. In the context of the present invention, the most important chain extenders for the above-identified TPUs are linear diols such as, for example, ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and hydroquinone bis(2-hydroxyethyl) ether. Exemplary of the
10 commercially available TPU thermoplastic elastomers include those available from DuPont (E. I. Du Pont de Nemours and Company, United States) under the tradename HYLENE, as well as those available from Morton (Morton International Specialty Chemicals) under the tradename IROGRAN.

The polyolefin-based thermoplastic elastomers (*i.e.*, TPOs) of the present
15 invention generally include random block copolymers (*e.g.*, ethylene α -olefin copolymers), block copolymers (*e.g.*, hydrogenated butadiene-isoprene-butadiene block copolymers), stereoblock polymers (*e.g.*, stereoblock polypropylene), graft copolymers (*e.g.*, polyisobutylene-g-polystyrene and EPDM-g-pivalolactone), and blends (*e.g.*, blends of ethylene-propylene random copolymer with isotactic polypropylene and
20 dynamically vulcanized blends of EPDM with a crystalline polyolefin). As is appreciated by those skilled in the art, all of these thermoplastic elastomers generally depend on crystallization of polymer chains to produce an elastomeric structure. For example, in the TPO random block copolymers (which are structurally similar to TPU random block copolymers) ethylene sequences long enough to crystallize at use
25 temperature act as physical crosslinks for the amorphous elastic chain segments. In the TPO stereoblock copolymers, changes in intrachain tacticity (*i.e.*, alternating stereoregularities) provide for the alternating crystalline and amorphous sequences. Furthermore, those skilled in the art recognize that many TPO thermoplastic elastomers embrace more than one thermoplastic elastomer classification as set forth above.

The thermoplastic elastomers based on halogen-containing polyolefins of the present invention include those thermoplastic elastomers having halogen atoms attached to the polymer backbone, as well as some blends of poly(vinyl chloride) (PVC) with crosslinked or elastomeric polymers. Exemplary in this regard is melt-processable rubber (MBR), as well as blends of PVC with acrylonitrile-butadiene elastomer (NBR), copolyester (CPO), and some thermoplastic polyurethane elastomers (TPUs).

The thermoplastic elastomers based on dynamically vulcanized elastomer-thermoplastic blends of the present invention are generally made through the relatively new processing technology referred to as "dynamic vulcanization". This proprietary processing technology has provided several novel thermoplastic elastomer materials (referred to herein as "thermoplastic vulcanizates") that have many properties as good or even, in some aspects, better than those of traditional styrenic block copolymers. Exemplary in this regard are the proprietary products prepared by the dynamic vulcanization of blends of olefin rubber with polyolefin resin such as those sold by Shell and Advanced Elastomer Systems (Shell Chemical Company, United States; Advanced Elastomer Systems, L.P., United States) under the tradename SANTOPRENE. Other thermoplastic vulcanizates, now generally referred to as TPVs, include various blends of ethylene-propylene-diene terpolymer (EPDM) elastomer with polypropylene and/or polyethylene, as well as blends of polyolefins with diene rubbers such as butyl rubber, natural rubber, acrylonitrile-butadiene copolymer (NBR), and styrene-butadiene copolymer (SBR).

The thermoplastic polyether ester elastomers of the present invention are generally multiblock copolyether esters with alternating, random-length sequences of either long-chain or short-chain oxyalkylene glycols connected by ester linkages. These materials are related structurally to the polyurethane and the polyamide thermoplastic elastomers in that they also contain repeating high-melting blocks that are capable of crystallization (hard segments) and amorphous blocks having a relatively low glass transition temperature (soft segments). Typically, the hard segments are composed of short-chain cyclic ester units such as teramethylene terephthalate, whereas the soft segments are generally derived from aliphatic polyether glycols. Exemplary of the

thermoplastic polyether ester elastomers are the polyether-ester block copolymers sold by DuPont (DuPont Engineering Polymers) under the tradename HYTREL.

The thermoplastic elastomers based on polyamides of the present invention are generally characterized as having a polyamide hard segment and an
5 aliphatic polyester, aliphatic polyether, and/or aliphatic polycarbonate soft segment. The polyamide-based thermoplastic elastomers, like the TPVs, are relative newcomers to the family of thermoplastic elastomers.

The styrenic thermoplastic elastomers of the present invention are generally characterized as polystyrene-polydiene block copolymers, where both ends of
10 each polydiene chain are terminated by polystyrene segments. With this type of thermoplastic elastomer, the rigid polystyrene domains act as multifunctional junction points to give a crosslinked elastomer network similar in some aspects to that of conventional vulcanized rubber. The polystyrene segments may include substituted polystyrene such as, for example, poly(α -methylstyrene), copolymers of α -
15 methylstyrene, and poly(*p*-*tert*-butyl-styrene), although these types of polystyrene segments are generally less preferred. In addition, the polydiene segments may include, for example, polyisoprene, polybutadiene, ethylene-propylene copolymers, and ethylene-butylene copolymers. Exemplary of the styrenic thermoplastic elastomers are those sold by Shell (Shell Chemical Company, United States) under the tradename
20 KRATON.

More specifically, the thermoplastic elastomer may comprise one or more styrenic block copolymers. Preferably, such styrenic block copolymers include one or more of a styrene-ethylene/butylene-styrene block copolymer (SEBS), a styrene-ethylene/propylene-styrene block copolymer (SEPS), a styrene-butadiene-styrene block
25 copolymer (SBS), and a styrene-isoprene-styrene block copolymer (SIS) (e.g., KRATON thermoplastic elastomer compounds, Shell Chemical Company, United States). In one embodiment, the thermoplastic elastomer of the present invention comprises a styrene-ethylene/butylene-styrene block copolymer (e.g., Tuftec, Asahi Chemicals, Japan). As is appreciated by those skilled in the art, SBS and SIS are A-B-
30 A type block copolymers having unsaturated elastomeric central segments, whereas

SEBS and SEPS are A-B-A type block copolymers having saturated elastomeric central segments. Accordingly, because of their structure, SBS and SIS are more sensitive to oxidation than SEBS and SEPS and are therefore less preferred.

5

3. Suitable Ethylene- α -olefin Copolymers

As noted above, the one or more above-identified thermoplastic elastomers may be compounded with one or more of an ethylene- α -olefin copolymer and/or a polypropylene polymer to yield a composition suitable for forming a primary synthetic closure adapted for sealable engagement and removable insertion into a bottle or container. In this regard, the one or more ethylene- α -olefin copolymers of the present invention generally comprise metallocene catalyzed ethylene- α -olefin copolymers, and more preferably, metallocene catalyzed ethylene- α -olefin copolymers selected from one or more of an ethylene-butene copolymer, an ethylene-hexene copolymer, and an ethylene-octene copolymer (any one of which may also be classified as a thermoplastic elastomer). In general, the alpha-olefin component of the ethylene- α -olefin copolymer ranges from 2% to 30% by weight of the copolymer. Moreover, the metallocene catalyzed ethylene- α -olefin copolymers have densities (gm/cc) generally ranging from 0.86 to 0.95, melt indexes (ASTM 1238) generally ranging from 0.2 to 30, and melting points ($^{\circ}$ C, by DSC) generally ranging from 50-120. In one embodiment, the metallocene catalyzed ethylene- α -olefin copolymer comprises an ethylene-octene copolymer (*e.g.*, Engage, Dupont Dow Elastomers, United States).

As is appreciated by those skilled in the art, polymers manufactured using metallocene based catalyst technology have only been commercially available since about the early 1990's. More importantly, however, is that metallocene polymerization technology now allows for the manufacturing of relatively high molecular weight copolymers of very specific tacticities (*e.g.*, isotactic and syndiotactic polymers), as well as the polymerization of almost any monomer - beyond the traditional C_3 to C_8 olefins - in an exact manner. (Note that a metallocene, as is

30

appreciated by those skilled in the art, is a positively charged metal ion sandwiched between two negatively charged cyclopentadienyl anions.)

In addition, those skilled in the art also recognize that ethylene- α -olefin copolymers, derived from metallocene based catalyst technology, include polyolefin
5 "plastomers" or POPs (the name given to Exxon's EXACT product line, which is manufactured with proprietary EXXPOL catalyst technology, Exxon Chemical, United States) and polyolefin "elastomers" or POEs (the name given to Dupont Dow Elastomer's ENGAGE product line, which is manufactured with its proprietary INSITE catalyst technology, Dupont Dow Elastomers LLC, United States). These new
10 polyolefin plastomers (POPs) and elastomers (POEs) are recognized as low molecular weight, linear low density ethylene- α -olefin copolymer made possible as a result of metallocene based catalyst technology. Moreover, any one of the above-identified ethylene- α -olefin copolymers, or combinations thereof, may be used in the various compositions of the present invention.

15

4. Suitable Polypropylene Polymers

As noted above, the one or more above-identified thermoplastic
20 elastomers and/or ethylene- α -olefin copolymers may be compounded with a polypropylene. As is appreciated by those skilled in the art, polypropylene is a polyolefin which is generally formed by low-pressure polymerization of propylene using an organometallic mixed catalyst (e.g., Ziegler-Natta catalyst); however, polypropylene may be formed by use of a metallocene catalyst. Polypropylene is
25 known to exist in three distinct structures: atactic polypropylene, syndiotactic polypropylene, and isotactic polypropylene. All three structures (and various combinations thereof) are suitable for the various compositions associated with the present invention.

With respect to atactic polypropylene, the methyl groups of each
30 propylene monomer are randomly disposed on either side of the stretched carbon chain - that is, the stereochemistry at the chiral centers is random. Such random atactic

polypropylene is generally produced by free-radical polymerization at high pressures. Because atactic polypropylene has an irregular stereochemistry, it is considered noncrystalline, has a low softening point, and generally has poor mechanical properties.

With respect to syndiotactic polypropylene, the methyl groups of each propylene monomer alternate regularly from one side of the stretched carbon chain to the other; whereas with isotactic polypropylene, the methyl groups of each propylene monomer are all on the same side of the stretched carbon chain. Accordingly, both syndiotactic and isotactic polypropylene have regular stereochemistries (*i.e.*, the stereochemistry at the chiral centers is ordered), and both are generally made using Ziegler-Natta catalysts. In addition, syndiotactic and isotactic polypropylene are generally much more crystalline than atactic polypropylene. That is, the regular arrangement of methyl groups along the stretched carbon chain allows them to fit together better in a crystal lattice structure. Without necessarily prescribing to any particularly scientific theory, it is believed that the higher crystallinity associated with syndiotactic and isotactic polypropylene allows for higher crystallinity in the formed synthetic closures of the present invention. Put differently, the higher degree of crystal lattice structure attributable to syndiotactic and isotactic polypropylene decreases the pathways (*e.g.*, interstitial gaps and irregularities) from which gases such as, for example, O₂, CO₂ and SO₂ may migrate through. For among these reasons, syndiotactic and isotactic polypropylene are generally preferred.

Thus, in other embodiments of the present invention, the thermoplastic elastomer and/or metallocene catalyzed ethylene- α -olefin copolymer are compounded with a polymer that comprises polypropylene, wherein the polypropylene is selected from one or more of a syndiotactic polypropylene and an atactic polypropylene. In one embodiment, the polypropylene comprises a syndiotactic polypropylene. (*e.g.*, Profax 6323, Montell Polyolefins, The Netherlands).

5. Suitable Additives

In order to optimize processability, the various thermoplastic elastomer blends may be compounded (albeit optionally) to a large extent with other polymers, and may also be compounded with various oils, plasticizers, fillers and extenders, as well as other specialty additives (collectively referred to as processing additives). Indeed, and as appreciated by those skilled in the polymer compounding art, any number of various processing additives may be added to enhance one or more physical characteristics and properties of the synthetic closures disclosed herein. Exemplary of such processing additives are those identified in Gächter R., Müller H., *The Plastics Additives Handbook*, 4th ed., Hanser Publishers, Munich, Germany (1996) (incorporated herein by reference in its entirety).

In some embodiments, the thermoplastic elastomer blends of the present invention are compounded with an extending oil that comprises a polyolefin oil. As used within the context of the present invention, the term "extending oil" includes carbonaceous materials added to the composition to reduce costs, or improve physical properties.

In still other embodiments, the thermoplastic elastomer materials of the present invention are compounded with a processing additive. As used within the context of the present invention, the term "processing additive" includes any additive that aids in the processing or workability of the materials and/or compositions to be formed into primary synthetic closures. For example, one or more other materials may be compounded with the overall composition so as to improve the composition's processability and/or performance characteristics of the primary closures. Thus, the term processing additives encompasses various oxygen scavengers that may be added to the overall composition (e.g., Daraform 25515-C-1, Darex Container Products, United States), as well as biological growth inhibitors useful in killing and/or preventing the proliferation of molds and bacteria. Other materials may also be compounded with the overall composition, such as coloring and flavoring agents, to thereby enhance the aesthetic and olfactory appeal of the primary synthetic closures.

In still further embodiments, the thermoplastic elastomer and/or metallocene catalyzed ethylene- α -olefin copolymer and/or polypropylene are also compounded with a polymer that comprises an ethylene-propylene copolymer (used to impart a higher degree of toughness). In addition, a "filler" such as calcium carbonate
5 and/or natural cork particles may also be compounded together with the one or more other ingredients to yield a suitable composition for making a synthetic closure.

6. Exemplary Compounding Techniques

10

As is appreciated by those skilled in the art, the above-identified ingredients (which are all associated with certain preferred embodiments of the present invention) may be compounded together as in the following exemplary manner. First, desired weight percentages of styrene-ethylene/butylene-styrene block copolymer,
15 polypropylene and ethylene- α -olefin copolymer, as well as desired amounts of processing additive or other specialty chemicals (*e.g.*, antioxidants, colorants, and stabilizers) may be added together in an appropriately sized first mixer (*e.g.*, 350 lb. Capacity Henschel Mixer w/cooler). This dry blend may then be mixed and allowed to reach a temperature of 80°F prior to feeding to an appropriately sized second
20 continuous mixer (*e.g.*, via a Colortronic MH 60 dosing feeder to a 4 inch Farrel Continuous Mixer). The blades of the second continuous mixer may then be rotated (*e.g.*, at 175 rpm) so as to cause the dry blend to flux into a homogeneous melt at an elevated temperature (*e.g.*, 340°F). The molten composition may then be transferred via
25 a transfer line jacketed with nitrogen to a single screw pelletizing extruder (*e.g.*, a single screw pelletizing extruder having a length to diameter ratio of 8 to 1). The molten composition may then be extruded through the die of the extruder (*e.g.*, a multi-hole die), cooled in a water bath, and strand cut through a cutter (*e.g.*, through a Cumberland cutter at a rate of 120-130 lbs. per hour). The resulting pellets are ready for manufacturing the various synthetic closures of the present invention.

30

7. Exemplary Synthetic Closure Manufacturing Processes

As is appreciated by those skilled in the art, the compounded ingredients (*e.g.*, pellets) of the present invention may be formed into primary synthetic closures by any number of suitable processing techniques. For example, the synthetic closures of the present invention may be formed by injection molding, extrusion, and casting. In one exemplary embodiment, a thermoplastic elastomer compounded with other polymers in accordance with the present invention is used as a feedstock for an injection molding process. In another exemplary embodiment, a thermoplastic elastomer compounded with other polymers in accordance with the present invention is used as a feedstock for an extrusion molding process (*e.g.*, the extrusion molding process described in U.S. Patent No. 5,904,965 to Noel *et al.*, which is incorporated herein by reference in its entirety).

In connection with an injection molding process, the feedstock is combined with a suitable blowing agent (*e.g.*, using automatic metering and mixing devices mounted directly on an injection molding machine), heated to a suitable temperature, and injected into a mold. The mold has a desired shape, such as, for example the shape of a wine cork. In some embodiments, the shape is that of a cylinder having a height of about 36.5 millimeters or about 44.5 millimeters, and a diameter of about 21.5 millimeters (*i.e.*, dimensions corresponding to that of two types of conventional wine closures), wherein the cylinder has a radius at an edge (*e.g.*, a rounded edge). The cylinder may, however, have either a chamfer or a bevel at an edge.

In still other embodiments, the compounded ingredients are mixed with a suitable blowing agent prior to the synthetic closure formation process (*e.g.*, injection molding or extrusion molding). As is appreciated by those skilled in the art, chemical blowing or foaming agents are additives which are able to evolve gas, such as N₂ or CO₂, through chemical reactions that produce foam structures in a polymeric matrix. Accordingly, in one embodiment, the blowing agent is an azodicarbonamide (or modified azocarbonamide) or a sodium bicarbonate, or mixture thereof (*e.g.*, Spectratech FM1150H, Quantum Chemical Corp., United States). The blowing agent generally comprises greater than 1% by weight of the total feedstock, and typically

comprises a range that includes at least 1.3%, 1.5% or 2.0% by weight of the total feedstock, and less than 9.0%, 5.0%, 4.0% or 3.0% by weight of the total feedstock. Thus, in one embodiment, the blowing agent comprises from about 1.3% to about 3.0%, typically from about 1.5% to about 2.5%, and preferably about 2.0% by weight of the
5 total feedstock.

In one exemplary synthetic closure manufacturing process, the feedstock and suitable blowing agent are allowed to form a mixture, which is generally injected into a cylindrical mold over a period of from about 0.02 to about 6 seconds, typically from about 0.03 to about 2 seconds, and preferably from about 0.04 to 1 second. The
10 molding pressure is generally from about 200 psi to about 900 psi, typically from about 300 psi to about 800 psi, and preferably from about 400 psi to about 700 psi. The molding temperature is generally from about 300°F to about 550°F, typically from about 325°F to about 425°F, and preferably from about 350°F to about 375°F, and further preferably about 350°F. The mixture is generally maintained in the mold from
15 about 20 seconds to about 90 seconds, typically from about 30 seconds to about 80 seconds, and preferably from about 35 to about 60 seconds. The injection molding process is preferably performed as quickly as practicable and with no special venting. After a time period sufficient for the overall composition to effectively harden within the mold, the mold is opened and the formed closure removed.

20 In a preferred embodiment, the mixture is injected into the mold at a rate and temperature such that the softened or molten mixture randomly coils about the mold, much like a string being lowered into a bottle, to produce a visible random curling pattern along the surface of the formed closure, as generally depicted in Figures 1 and 2. (Note that in Figure 3 the random twisting or curving pattern has been omitted
25 for purposes of better illustration of the embossed symbol.) In an alternative embodiment, the mixture is injected at a rate and temperature such the random curling pattern is minimized or even avoided (*e.g.*, Figure 3).

Furthermore, the air in the mold cavity at the beginning of a molding cycle is preferably removed by employing a vacuum assist coordinated with the
30 injection of the mixture. The vacuum assist may be applied for about the last second of

the injection period, or it may be first applied after the end of the injection period. Applying the vacuum assist too early in the injection period may result in overly large cell spaces within the formed closure, yielding an overly spongy product. Failure to employ a vacuum assist may result in increased molding cycle times.

5 As is appreciated by those skilled in the art, molding times, pressures, venting, cooling, vacuum assisting, product removal, and other factors relevant to injection molding will be based, to a large extent, upon the precise combination of materials included in the overall composition, as well as the type, size and shape of the mold.

10 For example, the precise amount of blowing agent used may be determined by one skilled in the art taking to account the exact composition of polymers and other ingredients used, as well as the injection or extrusion molding conditions. The use of too much blowing agent will generally result in a synthetic closure that has excessively large cells (*i.e.*, bubbles) in its interior, thus causing the
15 closure to be overly spongy and potentially inconsistent during production. The use of too little blowing agent will generally result in a synthetic closure that does not have enough cells or inadequately sized cells. Such a closure may be too hard for routine removal and reinsertion using, for example, a corkscrew, among other problems. With respect to cell size, in general, the average cell size of the foamed embodiments of the
20 present invention ranges from about 0.02 millimeters to about 0.50 millimeters, and the average cell density ranges from about 8,000 cells/cm³ to about 25,000 cells/cm³.

 In general, and in the case of an injection molding process, the number and size of the cells should in one preferred embodiment correspond to that of Figures 4A-C, whereas in the case of a co-extrusion molding process (wherein an inner formed
25 core has integrally bonded thereover an outer skin layer), the number and size of the cells should in other preferred embodiments correspond to that of Figures 5A-C and/or Figures 6A-C. The number and size of the cells notwithstanding, many of the synthetic closures of the present invention are manufactured such that they have structural features that allows them, when sealingly engaged within the cylindrical opening of a
30 wine bottle, to be removed with a normal corkscrew using a force of approximately

approximately 15 to 35 kn, and preferably from about 22 to 28 kn, and more preferably from about 24 to 26 kn.

5 8. Alternative T-Shaped Closure Embodiments

In still further embodiments, the synthetic closures of the present invention include bi-compositional closures that have an elastomeric shaft coupled to a hard plastic top (*e.g.*, a T-shaped closure). In these embodiments, the elastomeric shaft
10 is made from one of the compounded thermoplastic elastomer compositions disclosed herein. In contrast, the hard plastic top may be made from any suitable hard plastic, many varieties of which are well known in the art, such as an acrylonitrile-butadiene-styrene (ABS) (*e.g.*, Dow #478, Dow Chemicals, United States) and/or high impact polystyrene (HPS) (*e.g.*, Dow AIM 4800, Dow Chemicals, United States). Such bi-
15 compositional synthetic closures may be used, for example, as a bottle closure or stopper for liquor, wine, spirits and specialty foods, among other things.

The bi-compositional or "T-top" synthetic closures of the present invention may be produced by using a variety of known molding and joining methods. For example, the shaft portion of the synthetic cork may be formed by conventional
20 processing techniques such as injection molding, extrusion, vacuum forming, and solution casting. Preferably, the synthetic cork is made using co-injection molding equipment that injection molds two different types of materials at or about the same time. Thus, the co-injection molding equipment, and the process of using the same, molds the hard top and the elastomeric shaft as a single unit. Examples of bi-
25 compositional synthetic corks in accordance with the present invention are set forth in the Figures 7-9.

Referring to Figures 7A, 8A, and 9A, therein is shown a top perspective view of three representative synthetic corks each having a hard plastic top coupled to a thermoplastic elastomer shaft in accordance with the present invention. Specifically,
30 Figure 7A depicts a synthetic cork having a bulbous shaped hard plastic top; Figure 8A depicts a synthetic cork having a cylindrical shaped hard plastic top with a plurality of

longitudinal grooves on the outer circumference; and Figure 9A depicts a synthetic cork having a cylindrical shaped plastic hard top with a plurality of longitudinal ridges on the outer circumference. In each of these exemplary embodiments, the bulbous shape, the plurality of longitudinal grooves, and the plurality of longitudinal ridges, allow one to
5 more easily grip the synthetic cork, thereby facilitating removal and insertion of the synthetic cork into a suitable container or bottle.

Referring now to Figures 7B, 8B, and 9B, therein is shown a cross-sectional view taken substantially along line 1B-1B, line 2B-2B, and line 3B-3B of Figures 7A, 8A, and 9A, respectively. Specifically, each of these figures depicts a hard
10 plastic top having an extension, wherein the extension extends downwardly into the thermoplastic elastomer shaft. The extension portion of the hard plastic top allows the production of a more cost-effective product.

Referring now to Figures 7C, 8C, and 9C, therein is shown a cross-sectional view taken substantially along line 1C-1C, line 2C-2C, and line 3C-3C of
15 Figures 7B, 8B, and 9B, respectively. Specifically, each of these figures depicts a preferred shape of the extension and exemplary configurations of the interface between the hard plastic top and the thermoplastic elastomer shaft. The plurality of longitudinal cogs of the extension portion of the hard plastic top strengthens the coupling between thermoplastic shaft and hard plastic top.

20 As noted above, the bi-compositional synthetic corks of the present invention are typically used as a bottle closure or stopper for liquor, wine, spirits and specialty foods. These synthetic corks are particularly well suited for such use because such beverages and liquids are typically packaged in a bottle that is opened and closed several times over an extended period. For this reason, durability and sealing capability
25 are very important to the closure. The thermoplastic elastomer shaft is a strong material that provides superior properties for such uses, while the hard plastic top makes the closure easy to grasp, remove and reinsert. The co-injection molding process is also preferred both because of its cost-effectiveness, and because it permanently attaches the thermoplastic elastomer shaft to the hard plastic top, thereby allowing for multiple
30 openings and resealings of containers with reduced incidence of separation or breakage

of the shaft from the top (although other manufacturing processes can also provide such benefits). The bi-compositional synthetic corks of the present invention may be produced such that both the hard plastic top and the thermoplastic elastomer shaft are of the same color, or of different colors as desired.

5

EXAMPLES

In order to better illustrate the effectiveness of the novel compositions associated with the synthetic closures of the present invention, several exemplary synthetic closures were made and tested. The specific experimental materials, methods, and results are more fully set forth below. It is to be understood, however, that the following Examples 1-5 are provided for purposes of illustration, not restriction.

15

Example 1

A composition was formulated by combining three major polymeric components together with an extending oil and minor amounts of processing additives. Specifically, the composition was formulated by combining the following ingredients in the following weight percentages:

20

(1) 16.0% by weight of a high crystallinity polypropylene (Profax 6323, Montell Polyolefins, The Netherlands);

(2) 25.8% by weight of a styrene-ethylene/butylene-styrene block copolymer (Tuftec JT56F, Asahi Chemicals., Japan);

25

(3) 18.5% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 94, density 0.902, octene content 13.5% by weight, and melting point of 100°C. (Engage 8402, Dupont Dow Elastomers, United States);

30

(4) 18.5% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 96, density 0.913, octene content 9.0% by weight, and melting point of 107°C. (Engage 8403, Dupont Dow Elastomers, United States);

(5) 20.6% by weight of a polyolefin extending oil (Hydrobrite 380 PO);

and

(6) 0.6% by weight of processing additives (~ 0.56% Kemamide E, Witco Polymer Chemical Group, United States, and ~ 0.04% Irganox 1010, Ciba Specialty Chemicals, Switzerland).

The formulated composition (*i.e.*, compound no. 18S having approximately 20% PP, 33% TPE, and 47% ethylene- α -olefin copolymer) was found to have Shore A hardness 74. The formulated composition was combined with a blowing agent (Hydroceral CT 1131, B.I. Chemicals, United States) and injection molded at a temperature of about 350°F. The resulting synthetic closures were found to have excellent dimensional stability (*i.e.*, no "necking" or shrinkage), resilience, and internal cell structure. In addition, the synthetic closures were found to have a hard external skin.

15

Example 2

A composition was formulated by combining three major polymeric components together with an extending oil and minor amounts of processing additives. Specifically, the composition was formulated by combining the following ingredients in the following weight percentages:

(1) 11.0% by weight of a high crystallinity polypropylene (Profax 814, Montell Polyolefins, The Netherlands);

(2) 30.8% by weight of a styrene-ethylene/butylene-styrene block copolymer (Tuftec JT56F, Asahi Chemicals., Japan);

(3) 16.5% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 94, density 0.902, octene content 13.5% by weight, and melting point of 100°C. (Engage 8402, Dupont Dow Elastomers, United States);

(4) 16.5% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 96, density 0.913, octene content 9.0% by

30

weight, and melting point of 107°C. (Engage 8403, Dupont Dow Elastomers, United States);

(5) 24.6% by weight of a polyolefin extending oil (Hydrobrite 380 PO);

and

5 (6) 0.6% by weight of processing additives (~ 0.56% Kemamide E, Witco Polymer Chemical Group, United States, and ~ 0.04% Irganox 1010, Ciba Specialty Chemicals, Switzerland).

The formulated composition (*i.e.*, compound no. 20S having approximately 15% PP, 41% TPE, and 44% ethylene- α -olefin copolymer) was found to
10 have Shore A hardness 74. The formulated composition was then combined with a blowing agent (Hydroceral CT 1131, B.I. Chemicals, United States) and injection molded at a temperature of about 350°F. The resulting synthetic closures were found to have excellent dimensional stability (*i.e.*, no "necking" or shrinkage), resilience, and internal cell structure. In addition, the synthetic closures were found to have a hard
15 external skin.

Example 3

A composition was formulated by combining two major polymeric
20 components together with an extending oil and minor amounts of processing additives. Specifically, the composition was formulated by combining the following ingredients in the following weight percentages:

(1) 40.8% by weight of a styrene-ethylene/butylene-styrene block copolymer (Tuftec JT56F, Asahi Chemicals., Japan);

25 (2) 12.5% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 94, density 0.902, octene content 13.5% by weight, and melting point of 100°C. (Engage 8402, Dupont Dow Elastomers, United States);

(3) 12.5% by weight of a metallocene catalyzed ethylene-octene
30 copolymer having a Shore A hardness 96, density 0.913, octene content 9.0% by

weight, and melting point of 107°C. (Engage 8403, Dupont Dow Elastomers, United States);

(4) 32.6% by weight of a polyolefin extending oil (Hydrobrite 380 PO);

and

5 (5) 0.6% by weight of processing additives (~ 0.56% Kemamide E, Witco Polymer Chemical Group, United States, and ~ 0.04% Irganox 1010, Ciba Specialty Chemicals, Switzerland).

The formulated composition (*i.e.*, compound no. 9 having approximately 0% PP, 62% TPE, and 38% ethylene- α -olefin copolymer) was found to have Shore A
10 hardness 60. The formulated composition was then combined with a blowing agent (Hydroceral CT 1131, B.I. Chemicals, United States) and injection molded at a temperature of about 350°F. The resulting synthetic closures were found to have excellent dimensional stability (*i.e.*, no "necking" or shrinkage), resilience, and internal cell structure. In addition, the synthetic closures were found to have a hard external
15 skin.

Example 4

A composition was formulated by combining three major polymeric
20 components together with an extending oil and minor amounts of processing additives. Specifically, the composition was formulated by combining the following ingredients in the following weight percentages:

(1) 25.0% by weight of a high crystallinity polypropylene (Profax 6323, Montell Polyolefins, The Netherlands);

25 (2) 30.0% by weight of a styrene-ethylene/butylene-styrene block copolymer (Septon 8004, Kuraray Co. Ltd., Japan);

(3) 19.4% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 72, density 0.87, octene content 24.0% by weight, and melting point of 60°C. (Engage 8400, Dupont Dow Elastomers, United
30 States)

(4) 24.0% by weight of a polyolefin extending oil (Hydrobrite 380 PO);

and

(5) 1.6% by weight of processing additives (~ 1.5% Kemamide E, Witco Polymer Chemical Group, United States, and ~ 0.1% Irganox 1010, Ciba Specialty
5 Chemicals, Switzerland).

The formulated composition (*i.e.*, compound no. 2 having approximately 34% PP, 40% TPE, and 26% ethylene- α -olefin copolymer) was found to have Shore A hardness 84. The formulated composition was then combined with a blowing agent (Hydroceral CT 1131, B.I. Chemicals, United States) and injection molded at a
10 temperature of about 350°F. The resulting synthetic closures were found to have good dimensional stability (*i.e.*, no "necking" or shrinkage), resilience, and internal cell structure. In addition, the synthetic closures were found to have a hard but somewhat thinner external skin.

15

Example 5

A composition was formulated by combining three major polymeric components together with an extending oil and minor amounts of processing additives. Specifically, the composition was formulated by combining the following ingredients in
20 the following weight percentages:

(1) 5.0% by weight of a high crystallinity polypropylene (Profax 6323, Montell Polyolefins, The Netherlands);

(2) 40.8% by weight of a styrene-ethylene/butylene-styrene block copolymer (Tuftec JT56F, Asahi Chemicals, Japan);

25 (3) 10.0% by weight of a metallocene catalyzed ethylene-octene copolymer having a Shore A hardness 94, density 0.902, octene content 13.5% by weight, and melting point of 100°C. (Engage 8402, Dupont Dow Elastomers, United States);

(4) 10.0% by weight of a metallocene catalyzed ethylene-octene
30 copolymer having a Shore A hardness 96, density 0.913, octene content 9.0% by

weight, and melting point of 107°C. (Engage 8403, Dupont Dow Elastomers, United States);

(5) 32.6 % by weight of a polyolefin extending oil (Hydrobrite 380 PO);

and

5 (6) 0.6% by weight of processing additives (~ 0.56% Kemamide E, Witco Polymer Chemical Group, United States, and ~ 0.04% Irganox 1010, Ciba Specialty Chemicals, Switzerland).

The formulated composition (*i.e.*, compound no. 8 having approximately 8% PP, 62% TPE, and 30% ethylene- α -olefin copolymer) was found to have Shore A
10 hardness 62. The formulated composition was then combined with a blowing agent (Hydroceral CT 1131, B.I. Chemicals, United States) and injection molded at a temperature of about 350°F. The resulting synthetic closures were found to have excellent dimensional stability (*i.e.*, no "necking" or shrinkage), resilience, and internal cell structure. In addition, the synthetic closures were found to have a hard external
15 skin.

The several exemplary synthetic closures which were made and tested in accordance with Examples 1-5 as set forth above represent several discrete species that
20 define a broader genus. Stated somewhat differently, the formulated compositions associated with Examples 1-5 (*i.e.*, formulations comprising three major polymeric components) may be represented in terms of varying ranges associated with the composition, namely; a thermoplastic elastomer component ranging from 25% to 75% (weight basis); an ethylene- α -olefin copolymer component ranging from 15% to 65%
25 (weight basis); and a polypropylene polymer component ranging from 0% to 50% (weight basis). More succinctly, however, the polymeric materials that comprise the synthetic closures of some embodiments of the present invention may be represented as a compounded polymeric material that includes a thermoplastic elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer, wherein the relative amounts on a
30 weight percent basis of the thermoplastic elastomer, the ethylene- α -olefin copolymer,

and the polypropylene polymer vary with one another in the manner as set forth in the expression shown in Figure 10 (wherein the underlying polymeric compositions of Examples 1-5 have been plotted).

Moreover, synthetic closures of these blends and others were found to be superior over other known synthetic closures in the sense that they were able to better retain printed matter on their respective surfaces. Without necessarily prescribing to any particular scientific theory, it is believed that the relatively higher crystallinity associated with many of the polymeric compositions disclosed herein allowed for better surface retention of printed matter, because surface impinged ink particles are believed to be better trapped within the polymeric matrix associated with the skin portion of the closure.

While the products and methods of the present invention have been described in the context of the embodiments and related experimental data illustrated and described herein, the invention may be embodied in other specific ways or in other specific forms without departing from its spirit or essential characteristics. Therefore, the described embodiments and experimental data are to be considered in all respects only as illustrative and not restrictive. The scope of the present invention is, therefore, indicated by the appended claims rather than by the foregoing description, and all changes that come within the meaning and range of equivalency of the claims are to be embraced within their scope.

CLAIMS

We claim:

1. A synthetic closure for removable insertion into a bottle or container, wherein the closure is made from a composition formulated from the ingredients comprising:
a styrene block copolymer thermoplastic elastomer;
an ethylene- α -olefin copolymer;
a polypropylene polymer; and
a blowing agent.
2. The synthetic closure of claim 1 further comprising an extending oil.
3. The synthetic closure of claim 2 further comprising a processing additive.
4. The synthetic closure of claim 1 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene block copolymer, a styrene-ethylene/propylene-styrene block copolymer, a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, or a mixture thereof.
5. The synthetic closure of claim 1 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene block copolymer and a styrene-ethylene/propylene-styrene block copolymer, or a mixture thereof.
6. The synthetic closure of claim 1 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene block copolymer.
7. The synthetic closure of claim 1 wherein the ethylene- α -olefin copolymer is an ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, or a mixture thereof.

8. The synthetic closure of claim 1 wherein the ethylene- α -olefin copolymer is an ethylene-octene copolymer.

9. The closure of claim 1 wherein the polypropylene polymer is a syndiotactic polypropylene polymer and a isotactic polypropylene polymer, or a mixture thereof.

10. The closure of claim 1 wherein the polypropylene polymer is a syndiotactic polypropylene polymer.

11. The closure of claim 1 wherein the blowing agent is an azodicarbonamide compound.

12. A synthetic closure for removable insertion into a bottle or container comprising:

a styrene block copolymer thermoplastic elastomer, the thermoplastic elastomer ranging from 10% to 95% by weight of the composition;

a first polymer that comprises polypropylene, the first polymer ranging from 0% to 25% by weight of the composition;

a second polymer that comprises an ethylene- α -olefin copolymer, the second polymer ranging from 5% to 60% by weight of the composition; and

an extending oil that comprises a polyolefin, the extending oil ranging from 0% to 35% by weight of the composition.

13. The synthetic closure of claim 12 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene, a styrene-ethylene/propylene-styrene block copolymer, a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, or a mixture thereof.

14. The synthetic closure of claim 12 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene block copolymer, a styrene-ethylene/propylene-styrene block copolymer, or a mixture thereof.

15. The synthetic closure of claim 12 wherein the styrene block copolymer is a styrene-ethylene/butylene-styrene block copolymer.

16. The synthetic closure of claim 12 wherein the ethylene- α -olefin copolymer is an ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, or a mixture thereof.

17. The synthetic closure of claim 12 wherein the ethylene- α -olefin copolymer is an ethylene-octene copolymer.

18. The synthetic closure of claim 12 wherein the polypropylene polymer is a syndiotactic polypropylene polymer, an isotactic polypropylene polymer, or a mixture thereof.

19. The synthetic closure of claim 12 wherein the polypropylene polymer is a syndiotactic polypropylene polymer.

20. A synthetic closure adapted to sealingly engage a cylindrical opening of a wine bottle comprising a first thermoplastic vulcanizate.

21. The synthetic closure of claim 20 wherein the first thermoplastic vulcanizate is a dynamic vulcanized blend that includes an olefin rubber and a polyolefin resin.

22. The synthetic closure of claim 20 wherein the first thermoplastic vulcanizate is a dynamic vulcanized blend that includes an ethylene-propylene-diene terpolymer elastomer and a polypropylene.

23. The synthetic closure of claim 20 wherein the first thermoplastic vulcanizate is a dynamic vulcanized blend that includes an ethylene-propylene-diene terpolymer elastomer and a polyethylene.

24. The synthetic closure of claim 20 further comprising a thermoplastic elastomer, wherein the thermoplastic elastomer is different than the first thermoplastic vulcanizate.

25. The synthetic closure of claim 20 further comprising a polypropylene polymer.

26. The synthetic closure of claim 24 further comprising a polypropylene polymer.

27. The synthetic closure of claim 25 wherein the polypropylene polymer comprises a syndiotactic polypropylene polymer and an isotactic polypropylene polymer.

28. The synthetic closure of claim 25 wherein the polypropylene polymer is a syndiotactic polypropylene polymer.

29. The synthetic closure of claim 26 wherein the polypropylene polymer comprises a syndiotactic polypropylene polymer and an isotactic polypropylene polymer.

30. The synthetic closure of claim 26 wherein the polypropylene polymer is a syndiotactic polypropylene polymer.

31. The synthetic closure of claim 26 wherein the relative amounts of the thermoplastic elastomer, the first thermoplastic vulcanizate, and the polypropylene polymer vary with respect to one another on a weight percent in a manner wherein the thermoplastic elastomer ranges from 10% to 90%, the first thermoplastic vulcanizate ranges from 10% to 90%, and the polypropylene ranges from 0% to 50%.

32. The synthetic closure of claim 31 wherein the thermoplastic elastomer ranges from 30% to 70%, the first thermoplastic vulcanizate ranges from 30% to 70%, and the polypropylene ranges from 10% to 30%.

33. The synthetic closure of claim 31 wherein the thermoplastic elastomer is about 43%, the first thermoplastic vulcanizate is about 43%, and the polypropylene is about 14%.

34. The synthetic closure of claim 31 wherein the thermoplastic elastomer is an ethylene- α -olefin copolymer thermoplastic elastomer, a thermoplastic polyurethane elastomer, a polyolefin-based thermoplastic elastomer, a thermoplastic polyether ester elastomer, a styrene block copolymer thermoplastic elastomer, or a mixture thereof.

35. The synthetic closure of claim 34 wherein the thermoplastic elastomer is an ethylene- α -olefin copolymer thermoplastic elastomer.

36. The synthetic closure of claim 34 wherein the alpha-olefin component of the ethylene- α -olefin copolymer ranges from 2% to 30% by weight of the copolymer.

37. The synthetic closure of claim 35 wherein the ethylene- α -olefin copolymer thermoplastic elastomer is a metallocene catalyzed ethylene- α -olefin copolymer selected from one or more of an ethylene-butene copolymer, an ethylene-hexene copolymer, and an ethylene-octene copolymer.

38. The synthetic closure of claim 35 wherein the ethylene- α -olefin copolymer thermoplastic elastomer is a metallocene catalyzed ethylene-octene copolymer.

39. The synthetic closure of claim 34 wherein the thermoplastic elastomer is a thermoplastic polyurethane elastomer.

40. The synthetic closure of claim 34 wherein the thermoplastic elastomer is a polyolefin-based thermoplastic elastomer.

41. The synthetic closure of claim 34 wherein the thermoplastic elastomer is a thermoplastic polyether ester elastomer.

42. The synthetic closure of claim 34 wherein the thermoplastic elastomer is a styrene block copolymer thermoplastic elastomer.

43. The synthetic closure of claim 42 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer, a styrene-ethylene/propylene-styrene block copolymer, a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, or a mixture thereof.

44. The synthetic closure of claim 42 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer and a styrene-ethylene/propylene-styrene block copolymer, or a mixture thereof.

45. The synthetic closure of claim 42 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer.

46. The synthetic closure of claim 31 further comprising an extending oil.

47. The synthetic closure of claim 31 further comprising a processing additive.
48. The synthetic closure of claim 47 wherein the processing additive is an oxygen scavenger.
49. The synthetic closure of claim 31 further comprising a filler.
50. The synthetic closure of claim 49 wherein the filler is calcium carbonate.
51. The synthetic closure of claim 49 wherein the filler is natural cork particles.
52. The synthetic closure of claim 31 further comprising an ethylene-propylene copolymer.
53. A cylindrical shaped synthetic closure adapted for removable insertion into an opening of a wine bottle, wherein the synthetic closure has an inner foamed core structure surrounded by an outer skin layer that is of the same or different material than the inner foamed core structure, and wherein the synthetic closure is further adapted to sealingly engage the opening of the wine bottle, comprising a polymeric composition that includes a thermoplastic elastomer and a metallocene catalyzed ethylene- α -olefin copolymer.
54. The synthetic closure of claim 53 wherein the thermoplastic elastomer is one or more of an ethylene- α -olefin copolymer thermoplastic elastomer, a thermoplastic polyurethane elastomer, a polyolefin-based thermoplastic elastomer, a thermoplastic polyether ester elastomer, and a styrene block copolymer thermoplastic elastomer.

55. The synthetic closure of claim of claim 54 wherein the alpha-olefin component of the ethylene- α -olefin copolymer thermoplastic elastomer ranges from 2% to 30% by weight of the copolymer.

56. The synthetic closure of claim of claim 55 wherein the ethylene- α -olefin copolymer thermoplastic elastomer is a metallocene catalyzed ethylene- α -olefin copolymer selected from one or more of an ethylene-butene copolymer, an ethylene-hexene copolymer, and an ethylene-octene copolymer.

57. The synthetic closure of claim 56 wherein the ethylene- α -olefin copolymer thermoplastic elastomer is a metallocene catalyzed ethylene-octene copolymer.

58. The synthetic closure of claim 53 wherein the thermoplastic elastomer is a thermoplastic polyurethane elastomer.

59. The synthetic closure of claim 53 wherein the thermoplastic elastomer is a polyolefin-based thermoplastic elastomer.

60. The synthetic closure of claim 53 wherein the thermoplastic elastomer is a thermoplastic polyether ester elastomer.

61. The synthetic closure of claim 53 wherein the thermoplastic elastomer is a styrene block copolymer thermoplastic elastomer.

62. The synthetic closure of claim 61 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer, a styrene-ethylene/propylene-styrene block copolymer, a styrene-butadiene-styrene block copolymer, a styrene-isoprene-styrene block copolymer, or a mixture thereof.

63. The synthetic closure of claim 61 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer and a styrene-ethylene/propylene-styrene block copolymer, or a mixture thereof.

64. The synthetic closure of claim 61 wherein the styrene block copolymer thermoplastic elastomer is a styrene-ethylene/butylene-styrene block copolymer.

65. The synthetic closure of claim 53 wherein the metallocene catalyzed ethylene- α -olefin copolymer is an ethylene-butene copolymer, an ethylene-hexene copolymer, an ethylene-octene copolymer, or a mixture thereof.

66. The synthetic closure of claim 53 wherein the metallocene catalyzed ethylene- α -olefin copolymer is an ethylene-octene copolymer.

67. The synthetic closure of claim 53 further comprising a polypropylene polymer.

68. The synthetic closure of claim 67 wherein the polypropylene polymer comprises a syndiotactic polypropylene polymer and an isotactic polypropylene polymer.

69. The synthetic closure of claim 67 wherein the polypropylene polymer is a syndiotactic polypropylene polymer.

70. The synthetic closure of claim 53 further comprising an extending oil.

71. The synthetic closure of claim 53 further comprising a processing additive.

72. The synthetic closure of claim 71 wherein the processing additive is an oxygen scavenger.

73. The synthetic closure of claim 53 further comprising a filler.
74. The synthetic closure of claim 73 wherein the filler is calcium carbonate.
75. The synthetic closure of claim 73 wherein the filler is natural cork particles.
76. The synthetic closure of claim 53 further comprising an ethylene-propylene copolymer.
77. A cylindrical shaped synthetic closure adapted for removable insertion into an opening of a wine bottle, wherein the synthetic closure has an inner foamed core structure surrounded by an outer skin layer that is of the same or different material than the inner foamed core structure, and wherein the synthetic closure is further adapted to sealingly engage the opening of the wine bottle, comprising a thermoplastic polyurethane elastomer.
78. The synthetic closure of claim 77 wherein the thermoplastic polyurethane elastomer comprises a plurality of soft flexible segments and a plurality of hard segments, wherein the soft flexible segments comprise one or more long-chain polyols having an average molecular mass ranging from of 60 to 4,000 atomic mass units, and wherein the hard segments comprise one or more polyisocyanates.
79. The synthetic closure of claim 77 wherein the thermoplastic polyurethane elastomer comprises a plurality of soft flexible segments and a plurality of hard segments, wherein the soft flexible segments are hydroxyl terminated polyesters or hydroxyl terminated polyethers, and wherein the hard segments are selected from the group consisting of 4,4'-diphenylmethane diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane

diisocyanate, 3,3'-dimethyl-4,4'-biphenyl diisocyanate, 1,4-benzene diisocyanate, *trans*-cyclohexane-1,4-diisocyanate, and 1,5-naphthalene diisocyanate.

80. The synthetic closure of claim 77 further comprising a chain extender.

81. The synthetic closure of claim 80 wherein the chain extender is a linear diol.

82. The synthetic closure of claim 80 wherein the chain extender is selected from the group consisting of ethylene glycol, 1,4-butanediol, 1,6-hexanediol, and hydroquinone bis(2-hydroxyethyl) ether.

83. A method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of:

compounding a polymeric composition from the ingredients comprising a styrene block copolymer thermoplastic elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer;

combining the polymeric composition with a blowing agent under heat to yield a feedstock;

injecting the feedstock into a mold having a cylindrical shape; and

cooling the mold to form the synthetic closure.

84. A synthetic closure made in accordance with the process of claim 83.

85. A method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of:

combining a polymeric composition that comprises a thermoplastic vulcanizate with a blowing agent under heat to yield a feedstock;

injecting the feedstock into a mold having a cylindrical shape; and

cooling the mold to form the synthetic closure.

86. A synthetic closure made in accordance with the process of claim 85.

87. A method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of:

combining a polymeric composition that comprises a thermoplastic polyurethane elastomer with a blowing agent under heat to yield a feedstock;

injecting the feedstock into a mold having a cylindrical shape; and

cooling the mold to form the synthetic closure.

88. A synthetic closure made in accordance with the process of claim 87.

89. A method for manufacturing a synthetic closure adapted for removable insertion and sealable engagement with an opening of a wine bottle, comprising the steps of:

compounding a polymeric composition from the ingredients comprising a styrene block copolymer thermoplastic elastomer, an ethylene- α -olefin copolymer, and a polypropylene polymer;

combining the polymeric composition with a blowing agent under heat to yield a feedstock;

extruding or co-extruding the feedstock through a circular die to form a rod;

cooling the rod to yield a cooled rod; and

cutting the cooled rod to form the synthetic closure.

90. A synthetic closure made in accordance with the process of claim 89.

91. A wine bottle in combination with the synthetic closure of claim 1, 12, 20, 53, 77, 84, 86, 88, or 90.

1/11

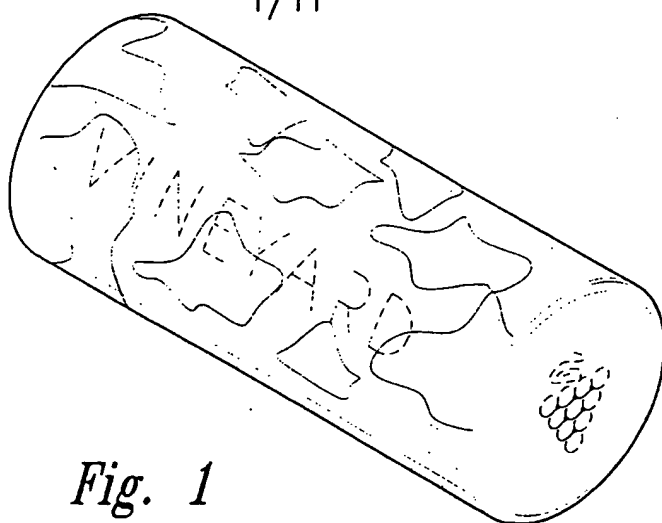


Fig. 1



Fig. 2

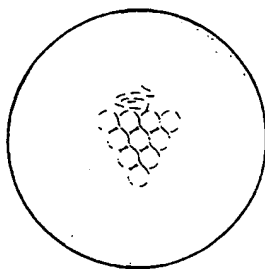
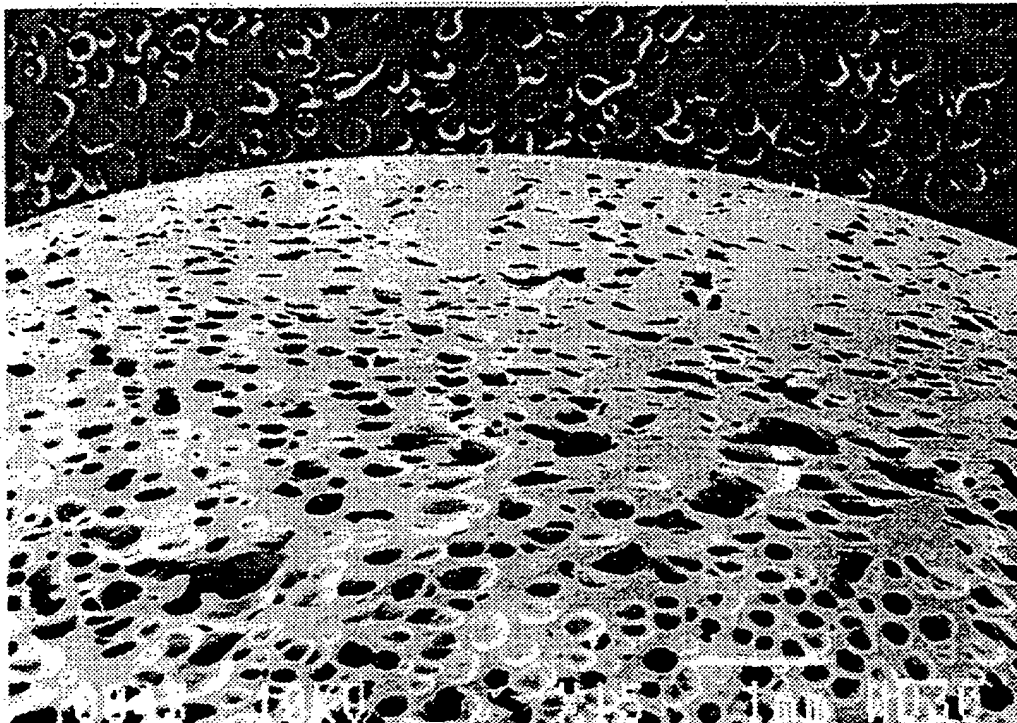
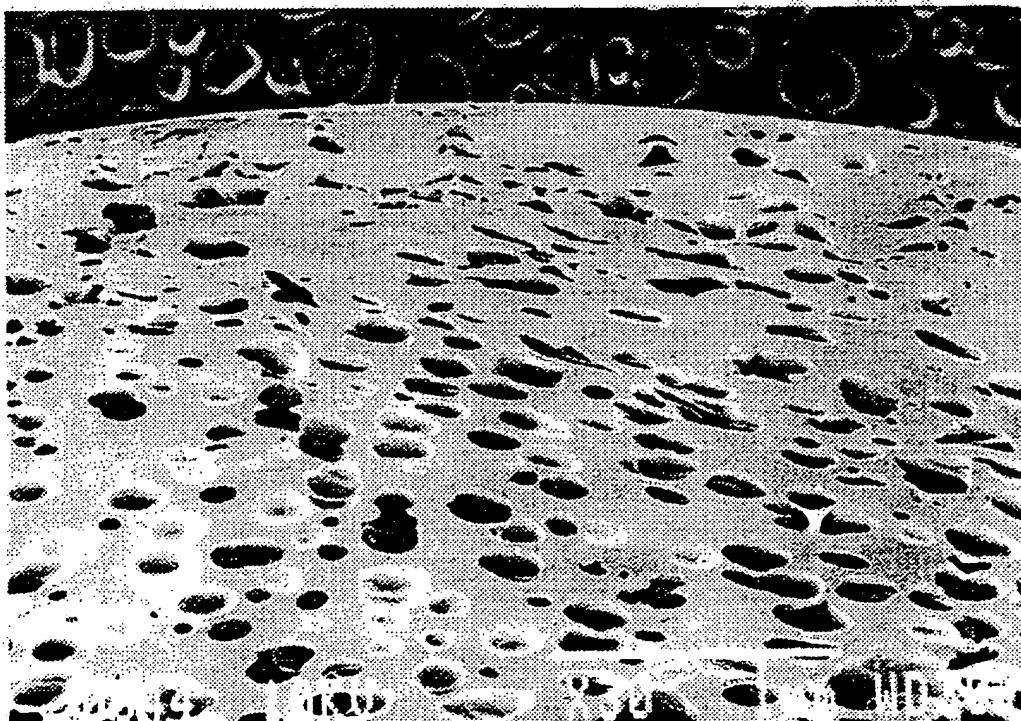


Fig. 3

*Fig. 4A**Fig. 4B*

3/11

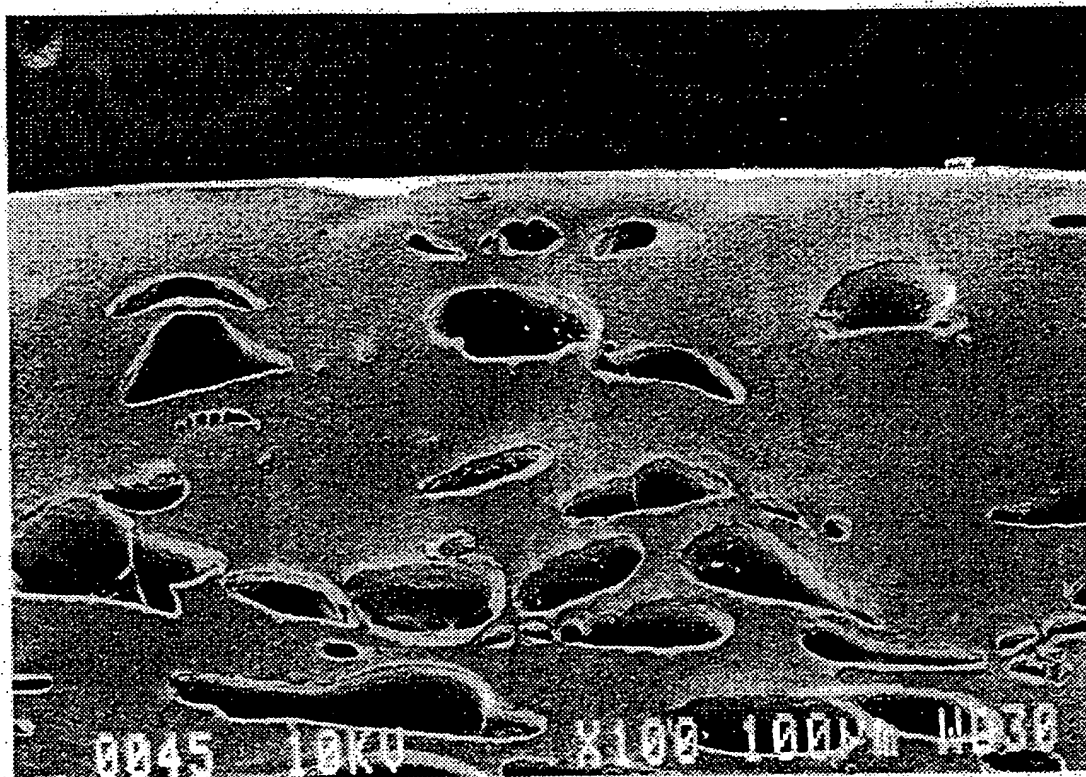


Fig. 4C

4/11

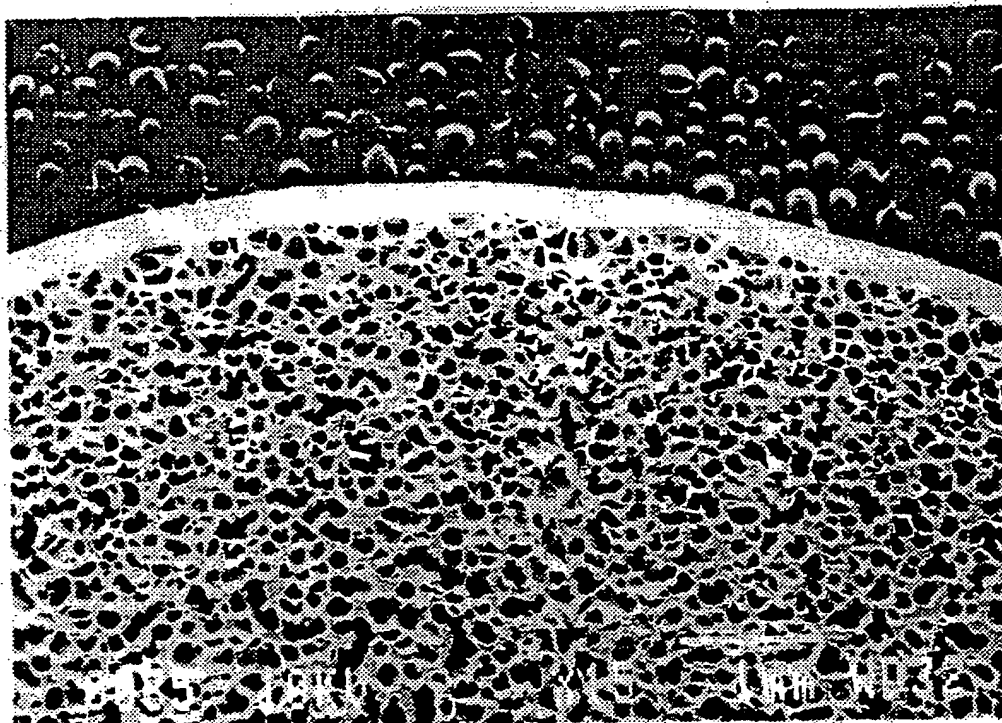


Fig. 5A

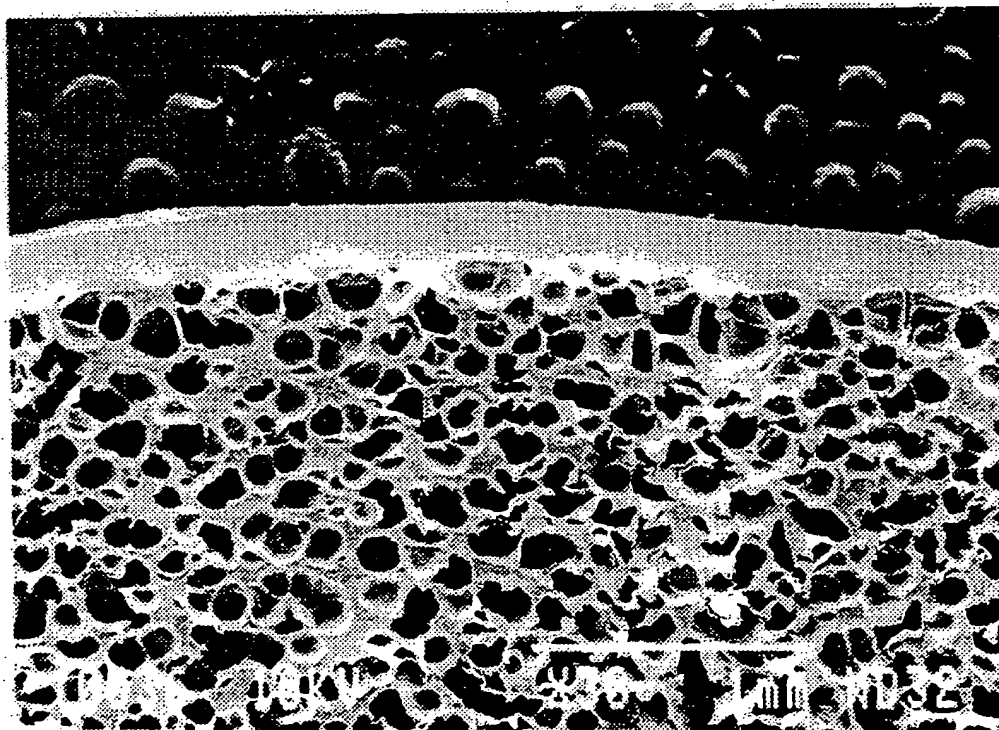


Fig. 5B

5/11

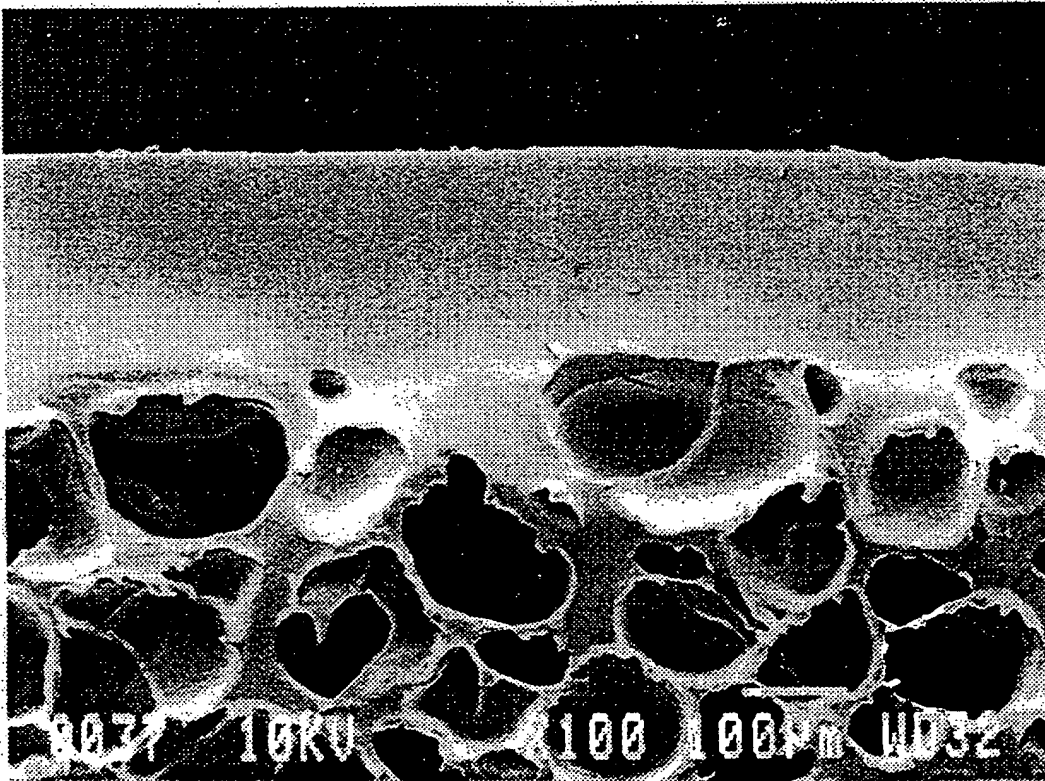


Fig. 5C

6/11

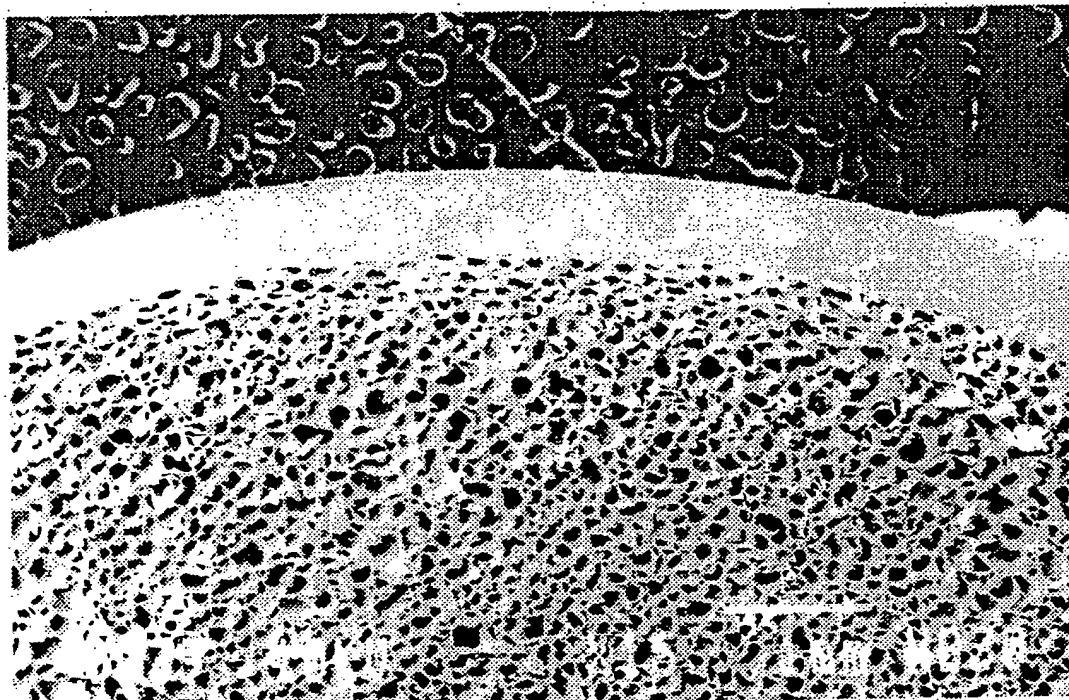


Fig. 6A

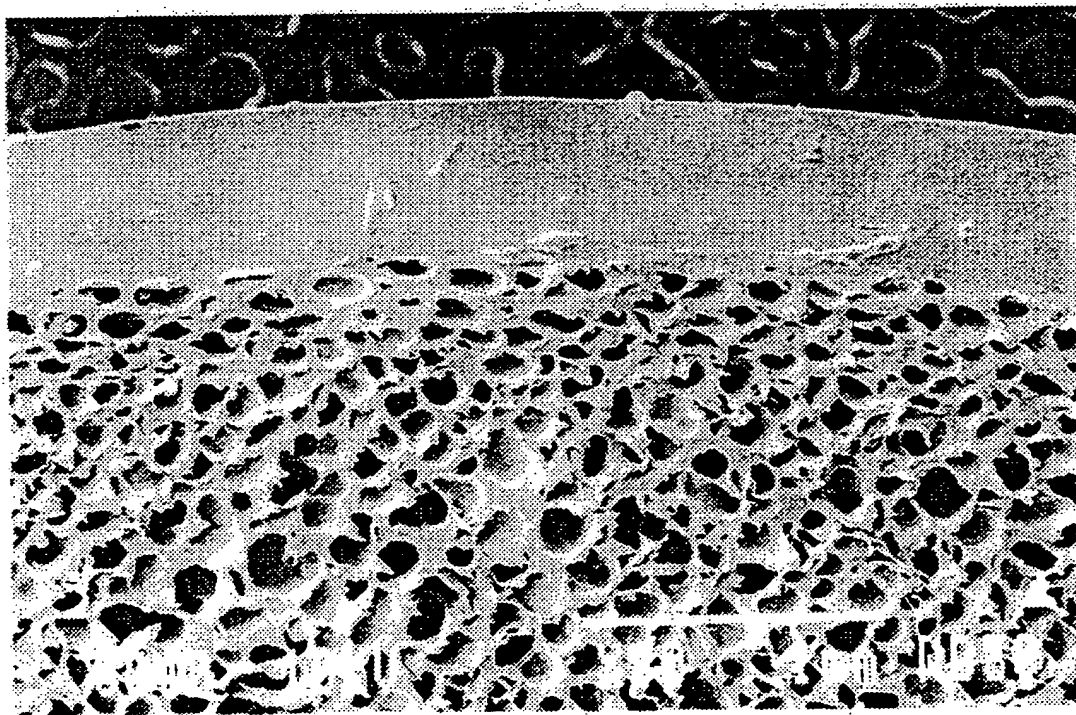


Fig. 6B

7/11

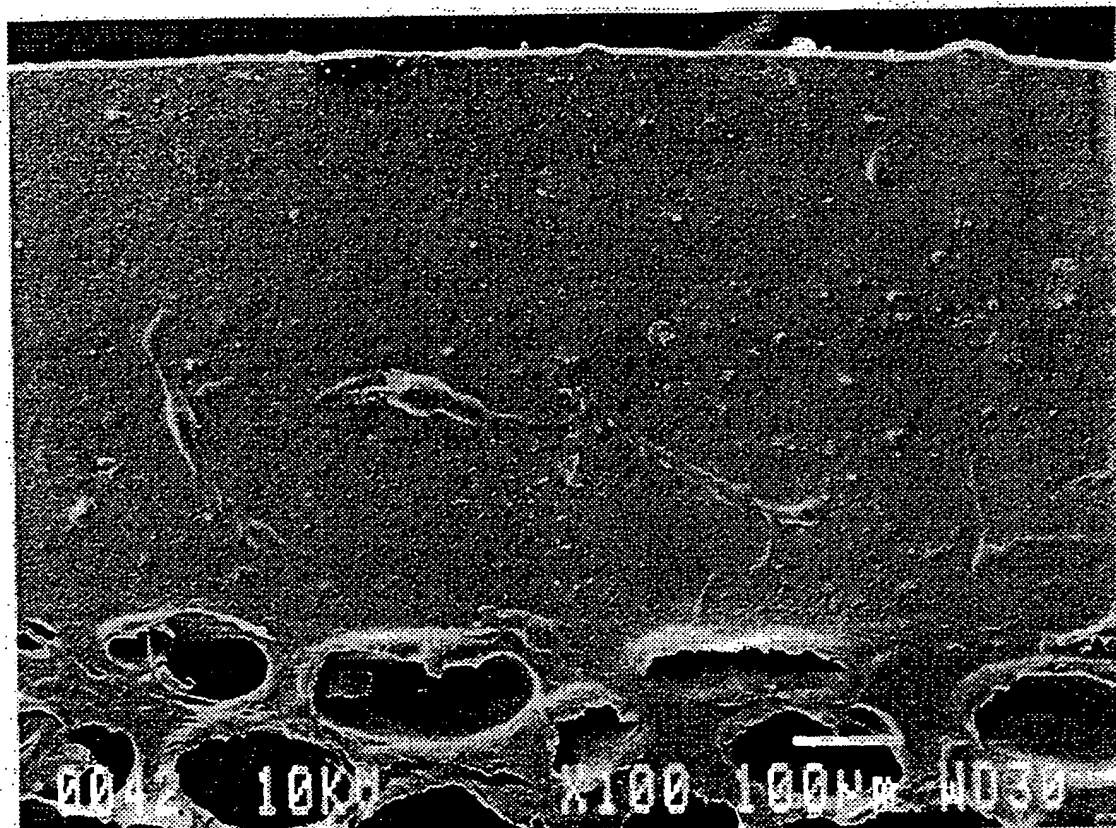


Fig. 6C

8/11

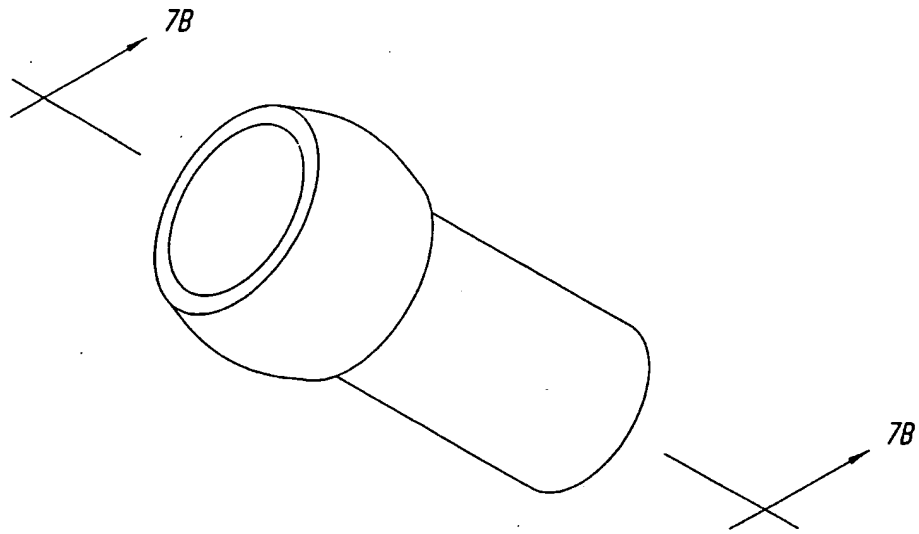


Fig. 7A

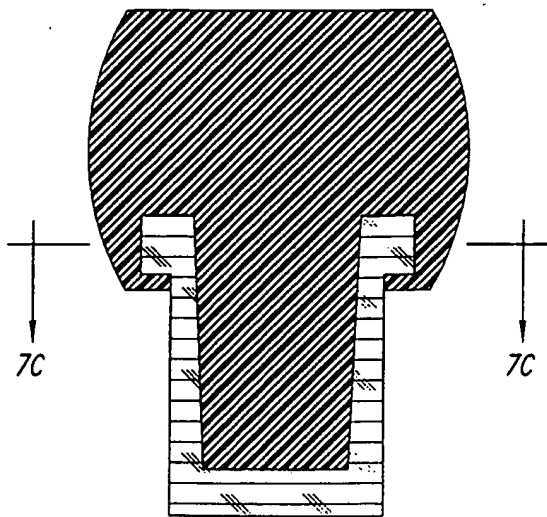


Fig. 7B

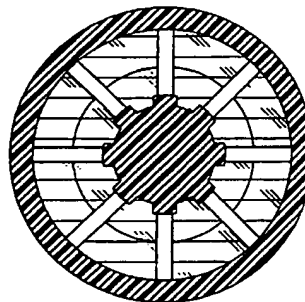


Fig. 7C

9/11

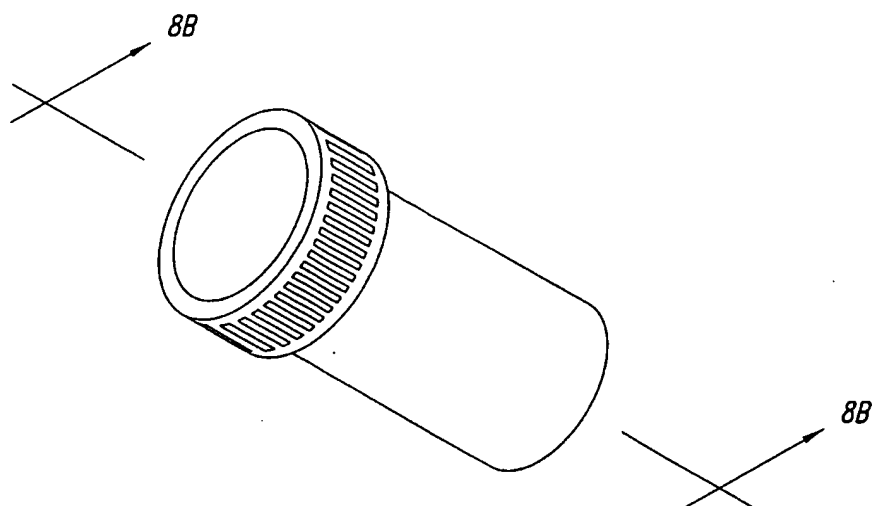


Fig. 8A

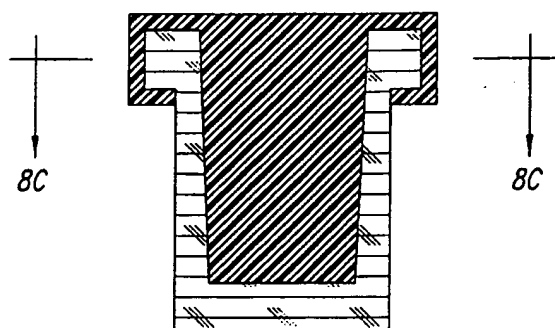


Fig. 8B

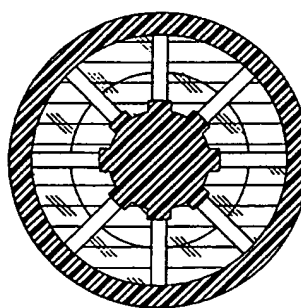


Fig. 8C

10/11

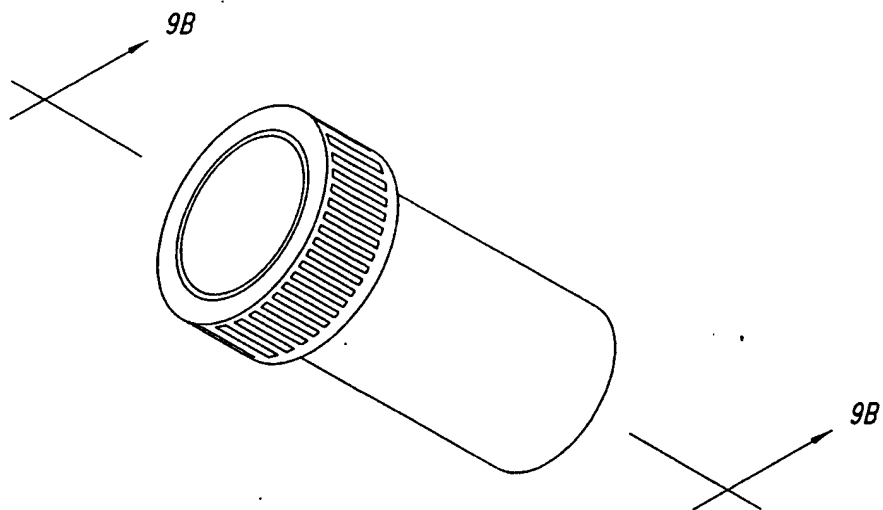


Fig. 9A

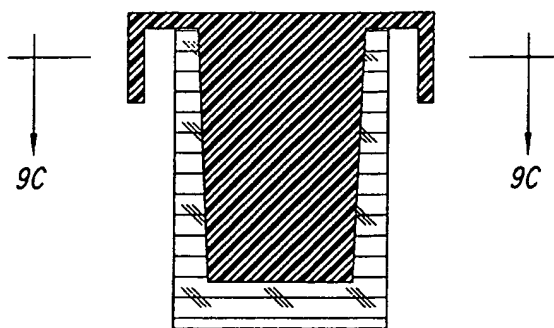


Fig. 9B

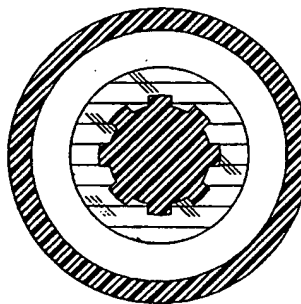
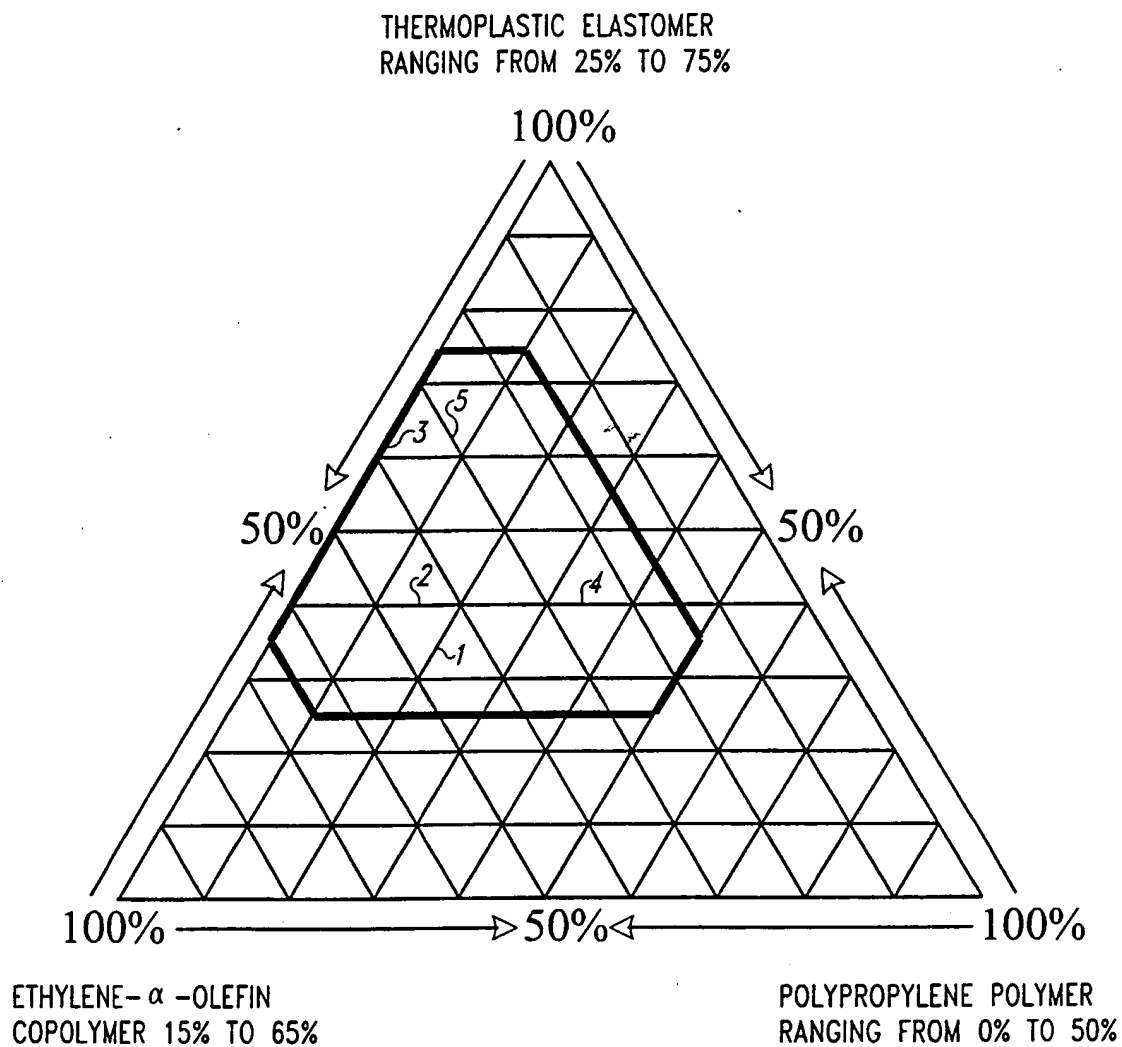


Fig. 9C

11/11

*Fig. 10*

INTERNATIONAL SEARCH REPORT

Internat'l Application No

PCT/US 99/25862

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 B65D39/00 C08J9/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B65D C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X, P A	US 5 855 287 A (BURNS DENNIS L) 5 January 1999 (1999-01-05) cited in the application the whole document	1-6, 11, 20, 83-89, 91 7, 9, 12-16, 18, 53, 77, 90, 91
X A	US 4 499 141 A (PAISLEY GARY V ET AL) 12 February 1985 (1985-02-12) the whole document	1-3, 12, 20, 53, 77, 91 83-90
A	US 5 692 629 A (BURNS DENNIS L) 2 December 1997 (1997-12-02) cited in the application the whole document	1-6, 12-16, 20, 53, 77, 83-91

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

*** Special categories of cited documents :**

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"a" document member of the same patent family

Date of the actual completion of the international search

21 February 2000

Date of mailing of the international search report

28/02/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
 Fax (+31-70) 340-3016

Authorized officer

SERRANO GALARRAGA, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Application No

PCT/US 99/25862

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5855287 A	05-01-1999	US 5480915 A	02-01-1996
		US 5496862 A	05-03-1996
		US 5692629 A	02-12-1997
		US 5710184 A	20-01-1998
		AU 2387099 A	10-06-1999
		AU 691497 B	21-05-1998
		AU 6783894 A	21-11-1994
		BG 100118 A	31-07-1996
		BR 9406394 A	13-02-1996
		CA 2161673 A	10-11-1994
		CN 1124968 A	19-06-1996
		CZ 9502880 A	14-02-1996
		EP 0698054 A	28-02-1996
		FI 955287 A	03-01-1996
		HU 73270 A	29-07-1996
		JP 9500074 T	07-01-1997
		NO 954417 A	03-01-1996
		NZ 266368 A	26-11-1996
		PL 311642 A	04-03-1996
		SK 136995 A	04-12-1996
		WO 9425513 A	10-11-1996
US 4499141 A	12-02-1985	US 4363849 A	14-12-1982
		AT 15163 T	15-09-1985
		AT 57665 T	15-11-1990
		AU 552342 B	29-05-1986
		AU 7669581 A	06-05-1982
		BG 50383 A	15-07-1992
		BR 8106897 A	13-07-1982
		CA 1177600 A	06-11-1984
		CS 8107998 A	13-06-1985
		EP 0051277 A	12-05-1982
		EP 0156957 A	09-10-1985
		ES 506677 A	01-06-1983
		ES 515420 A	16-01-1984
		GR 76316 A	04-08-1984
		HU 201698 B	28-12-1990
		IE 56508 B	28-08-1991
		IE 56507 B	28-08-1991
		IL 79596 A	28-02-1989
		JP 1401622 C	28-09-1987
		JP 57103826 A	28-06-1982
		JP 62001809 B	16-01-1987
		KR 8600419 B	19-04-1986
		MX 161007 A	29-06-1990
		NZ 198810 A	31-05-1985
		PL 233643 A	27-09-1982
		PT 73896 A,B	01-11-1981
		YU 258381 A	31-12-1983
		ZA 8107139 A	29-09-1982
US 5692629 A	02-12-1997	US 5480915 A	02-01-1996
		US 5496862 A	05-03-1996
		US 5710184 A	20-01-1998
		US 5855287 A	05-01-1999
		AU 2387099 A	10-06-1999
		AU 691497 B	21-05-1998
		AU 6783894 A	21-11-1994

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/US 99/25862

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5692629 A		BG 100118 A	31-07-1996
		BR 9406394 A	13-02-1996
		CA 2161673 A	10-11-1994
		CN 1124968 A	19-06-1996
		CZ 9502880 A	14-02-1996
		EP 0698054 A	28-02-1996
		FI 955287 A	03-01-1996
		HU 73270 A	29-07-1996
		JP 9500074 T	07-01-1997
		NO 954417 A	03-01-1996
		NZ 266368 A	26-11-1996
		PL 311642 A	04-03-1996
		SK 136995 A	04-12-1996
		WO 9425513 A	10-11-1996

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☒ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.